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# EVALUATION OF POLLUTION CONTROL IN FOSSIL FUEL CONVERSION PROCESSES. GASIFICATION; SECTION I: $CO_2$ ACCEPTOR PROCESS

C. E. Jahnig, et al

Exxon Research and Engineering Company

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The report gives results of a review of the CO2 Acceptor Coal Gasification Process from the standpoint of its effect on the environment. The quantities of solid, liquid, and gaseous effluents have been estimated, where possible, as well as the thermal efficiency of the process. For the purpose of reducing environmental impact, a number of possible process modifications or alternatives have been proposed and new technology needs have been pointed out.

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# EVALUATION OF POLLUTION CONTROL IN FOSSIL FUEL CONVERSION PROCESSES

## GASIFICATION; SECTION I: $CO_2$ ACCEPTOR PROCESS

by

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## SUMMARY

The $CO_2$ Acceptor Coal Gasification Process has been reviewed from the standpoint of its effect on the environment. The quantities of solid, liquid and gaseous effluents have been estimated, where possible, as well as the thermal efficiency of the process. For the purpose of reducing environmental impact, a number of possible process modifications or alternatives have been proposed and new technology needs have been pointed out.

## INTRODUCTION

Along with improved control of air and water pollution, the country is faced with urgent needs for energy sources. To improve the energy situation, intensive efforts are under way to upgrade coal, the most plentiful domestic fuel, to liquid and gaseous fuels which give less pollution. Other processes are intended to convert liquid fuels to gas. A few of the coal gasification processes are already commerically proven, and several others are being developed in large pilot plants. These programs are extensive and will cost millions of dollars, but this is warranted by the projected high cost for commercial gasification plants and the wide application expected in order to meet national needs. Coal conversion is faced with potential pollution problems that are common to coal-burning electric utility power plants in addition to pollution problems peculiar to the conversion process. It is thus important to examine alternative conversion processes from the standpoint of pollution and thermal efficiencies and these should be compared with direct coal utilization when applicable. This type of examination is needed well before plans are initiated for commercial applications. Therefore, the Environmental Protection Agency arranged for such a study to be made by Exxon Research & Engineering Company under contract EPA-68-02-0629, using all available non-proprietary information.

The present study under the contract involves preliminary design work to assure the processes are free from pollution where pollution abatement techniques are available, to determine the overall efficiency of the processes and to point out areas where present technology and information are not available to assure that the processes are non-polluting. This is one of a series of reports on different fuel conversion processes.

All significant input streams to the processes must be defined, as well as all effluents and their compositions. This requires complete mass and energy balances to define all gas, liquid, and solid streams. With this information, facilities for control of pollution can be examined and modified as required to meet Environmental Protection Agency objectives. Thermal efficiency is also calculated, since it indicates the amount of waste heat that must be rejected to ambient air and water and is related to the total pollution caused by the production of a given quantity of clean fuel. Suggestions are included concerning technology gaps that exist for techniques to control pollution or conserve energy. Maximum use was made of the literature and information available from developers. Visits with some of the developers were made, when it appeared warranted, to develop and update published information. Not included in this study are such areas as cost, economics, operability, etc. Coal mining and general offsite facilities are not within the scope of this study.

Considerable assistance was received in making this study, and we wish to acknowledge the help and information furnished by EPA and The Conoco Coal Development Company (formerly the Consolidation Coal Company).

## TABLE OF CONVERSION UNITS

| To Convert From | To | Multiply By |
|---|---|---|
| Btu | Calories | 0.25198 |
| Btu/pound | Calories, kilogram | 0.55552 |
| Cubic feet/day | Cubic meters/day | 0.028317 |
| Feet | Meters | 0.30480 |
| Gallons/minute | Cubic meters/minute | 0.0037854 |
| Inches | Centimeters | 2.5400 |
| Pounds | Kilograms | 0.45359 |
| Pounds/Btu | Kilograms/calorie | 1.8001 |
| Pounds/hour | Kilograms/hour | 0.45359 |
| Pounds/square inch | Kilograms/square centimeter | 0.070307 |
| Tons | Metric tons | 0.90719 |
| Tons/day | Metric tons/day | 0.90719 |

# 1. PROCESS DESCRIPTION AND EFFLUENTS

## 1.1 $CO_2$ Acceptor Process - General

This process makes synthetic natural gas (SNG) from lignite by gasifying it with steam at 1500°F and 150 psig. Heat is supplied indirectly by circulating dolomite which also takes up $CO_2$ and sulfur. After clean-up to remove dust and sulfur, the gas is methanated, giving a heating value of 952 Btu/cf HHV. Since the gas fed to methanation has a high hydrogen content, it requires no shifting or $CO_2$ removal ahead of the methanator. It is compressed and dried to meet pipeline requirements.

The $CO_2$ Acceptor Process has been operated in large pilot facilities and is described in the literature (1,2,3). The basis as supplied by the developer is shown in Figures 1 and 2, Tables 1 and 2 and Reference (3). The plant is sized to make 250 x $10^9$ Btu/day (262.6 MM SCFD) of pipeline gas. Additions were made as required to control pollution, and to arrive at a complete picture with all effluent streams defined, according to available data, together with utilities balances for steam, power, and water. Results of the study are summarized in the overall flowplan on Figure 3, while all input and effluent streams are shown in Figure 4 and Table 3.

The $CO_2$ Acceptor Process has been operated on lignite but is not considered operable on Eastern coal because higher temperatures are needed to get reasonable reaction rates. The higher system pressure needed to give enough $CO_2$ partial pressure in the gasifier results in a higher regenerator temperature which would be needed to calcine the acceptor, and, which in turn would cause slagging of the fuel char ash as well as severe loss of acceptor activity.

Raw lignite containing 33.67% moisture is supplied to the plant and is dried and preheated to 500°F. Heat for this operation increases the lignite feed requirement by 8-9%. Preheated lignite is raised to system pressure using lock hoppers. All lift gas and other gas used in this system is collected and returned through the dryer and bag filters for clean-up before release to the air.

The lignite is gasified with steam in a fluid bed reactor at 1500°F and the developer indicates that negligible tar or phenols are formed during normal operation, based on pilot plant results. However, there may be some during process upsets. Steam feed is preheated to 1200°F and steam conversion in the gasifier is about 70%. One-fourth of the heat required in the gasifier is supplied by sensible heat in the circulating dolomite returned at 1850°F, while the remainder comes from the heat of reaction when the dolomite takes up $CO_2$.

Raw gas from the reactor is passed through a waste heat boiler to generate steam and is then scrubbed to remove dust and ammonia. There may also be some tar, phenols, etc., during start-up or upsets, and therefore provision for handling them is included. In the acid gas removal unit, sulfur is removed to protect the methanation catalyst, and a minor amount of $CO_2$ is taken out so that the total amount of carbon

Figure 1

COAL PREPARATION

Flow Plan by Consolidation Coal Co.

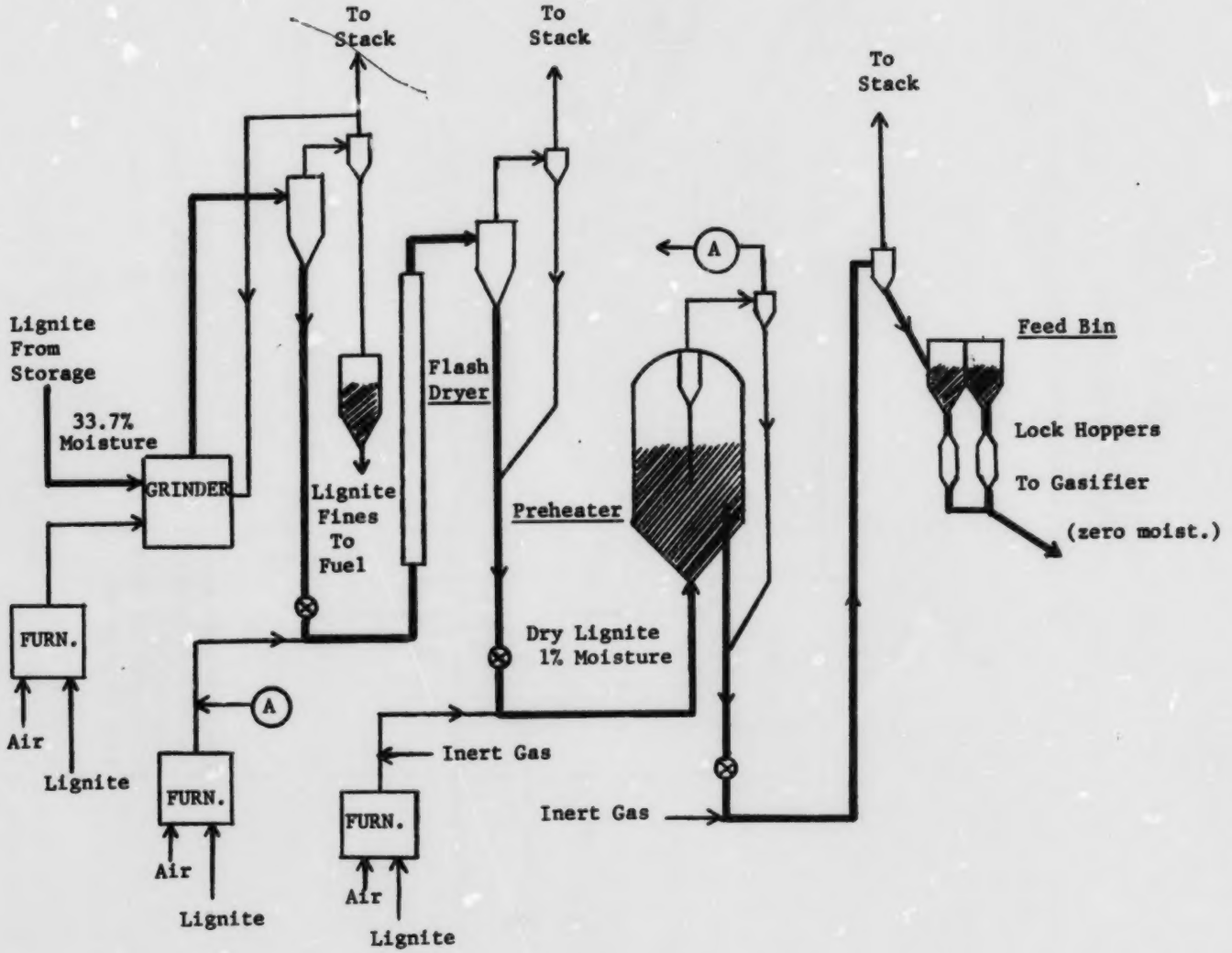


Figure 2

GASIFICATION SECTION

Design Basis by Consolidation Coal Co.

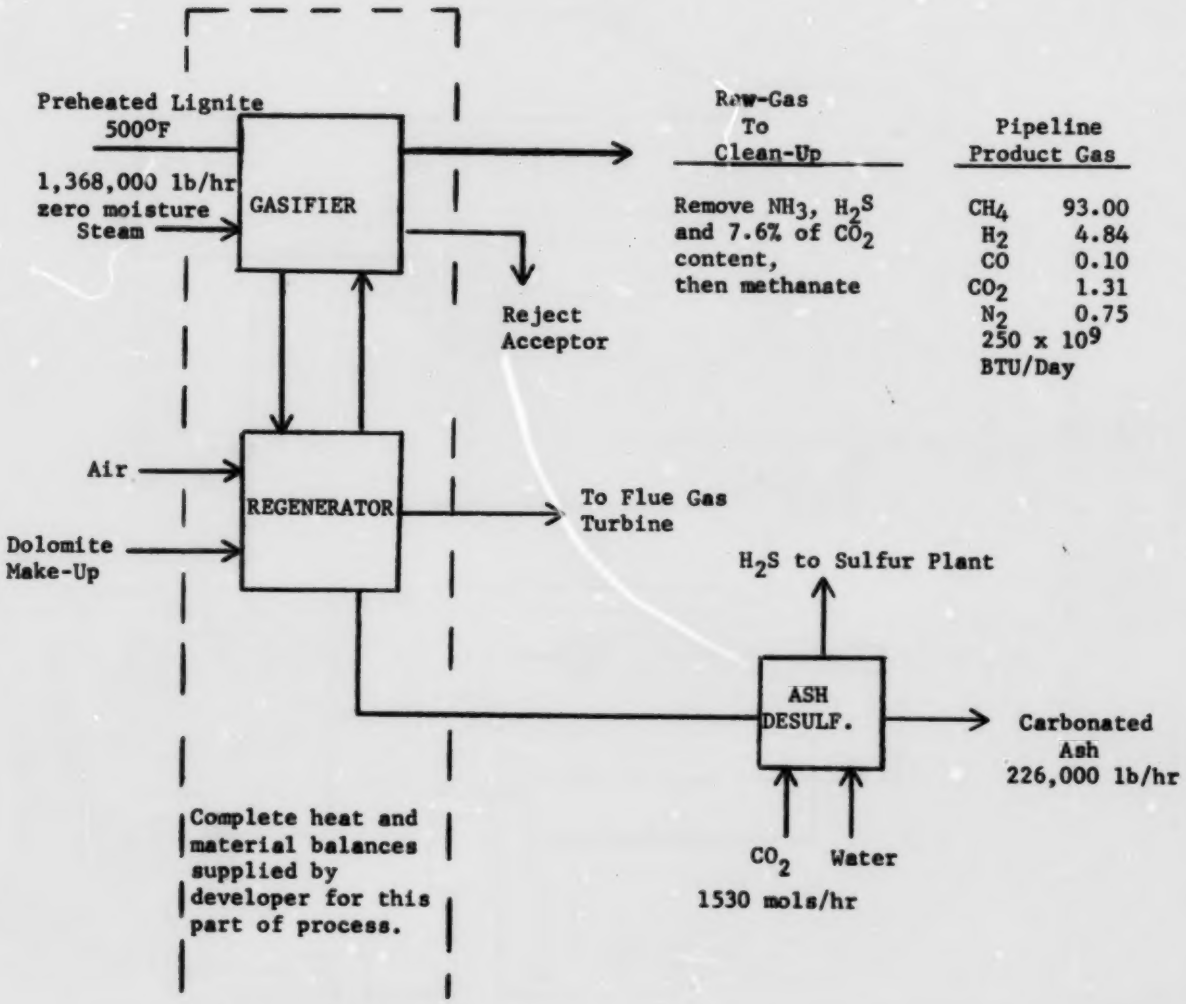


Figure 3

$CO_2$ Acceptor Process with Modifications to Reduce Emissions

Block Flow Diagram to Show Major Streams for Complete Plant Including Auxiliary Facilities

Basis: 250 x $10^9$ Btu/day of Pipeline Gas

(Numbers are lb/hr except where indicated.)

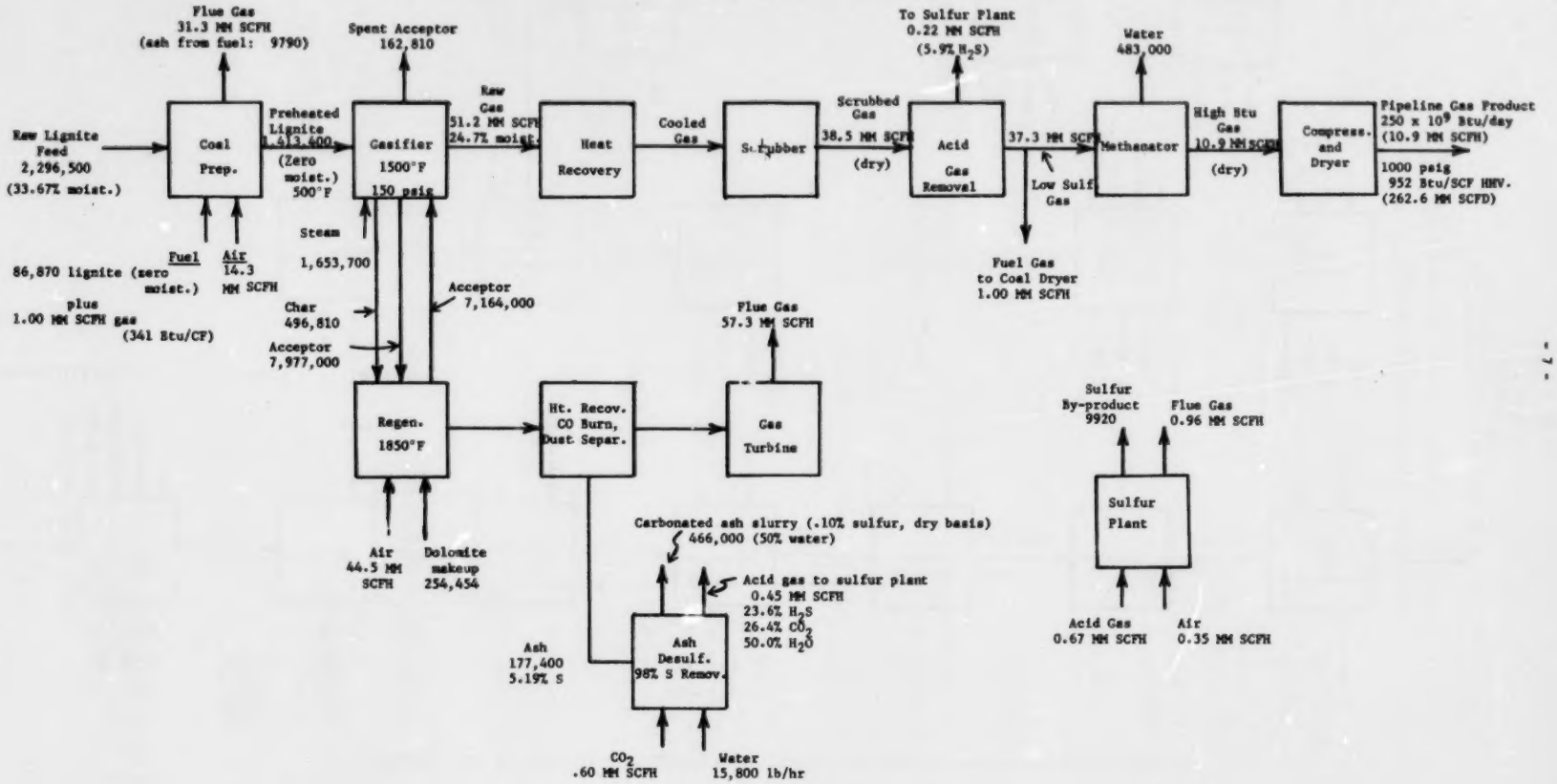
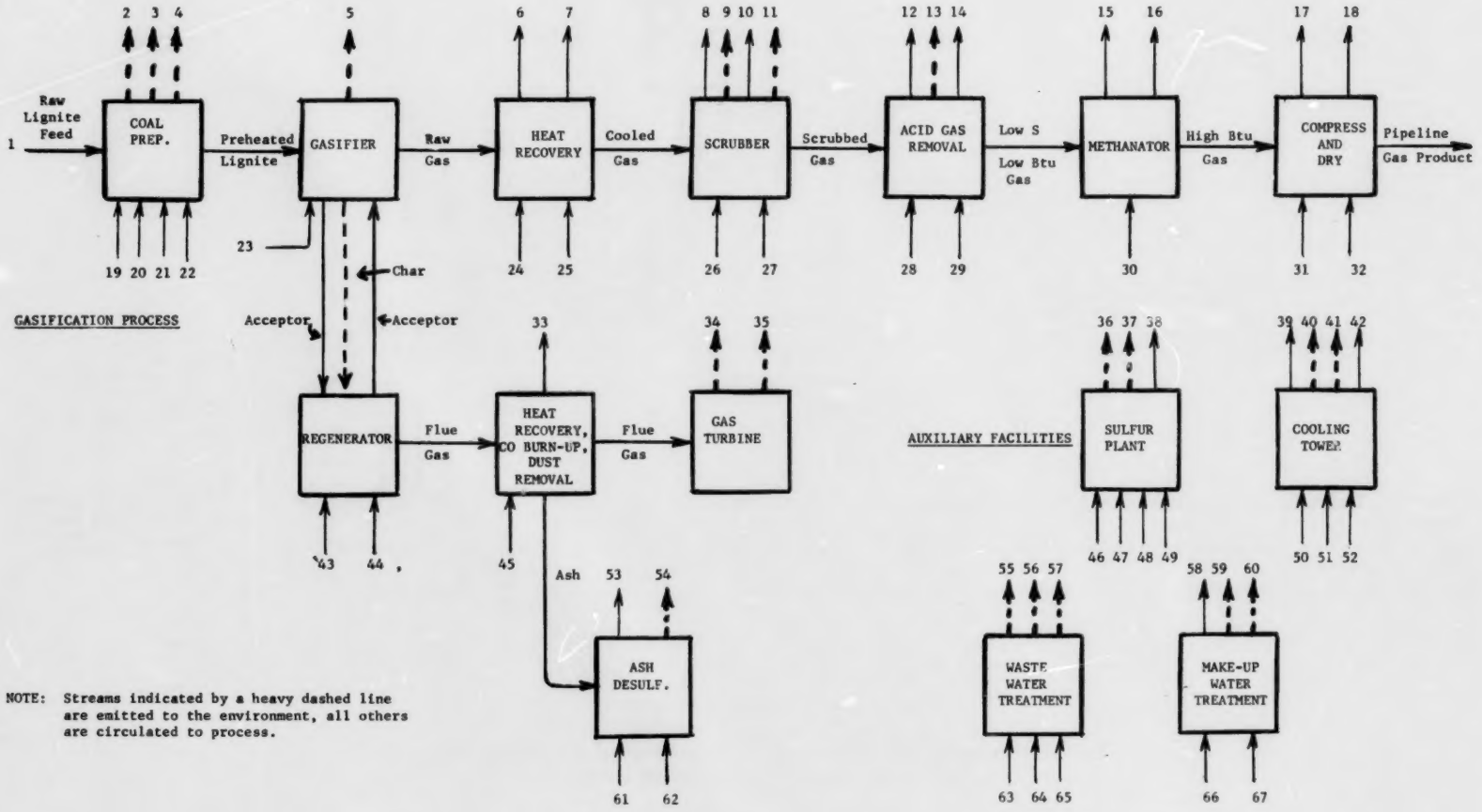


Figure 4

$CO_2$ ACCEPTOR PROCESS FOR COAL GASIFICATION

Design Revised To Incorporate Environmental Controls And All Streams Including Auxiliary Facilities




NOTE: Streams indicated by a heavy dashed line are emitted to the environment, all others are circulated to process.

# TABLE 1
## $CO_2$ ACCEPTOR PROCESS (4)

### Gasifier Heat and Material Balance
### System Pressure, 150 psig

Basis: 100 lb dry lignite fed to gasifier *
Datum: 60°F, liquid water

| | Lbs. | Mols | Mol % | °F | Enthalpy, Btu | Ht. of Combustion, Btu |
|---|---|---|---|---|---|---|
| **Input** | | | | | | |
| Preheated Lignite(1) | 100 | | | 500 | 14,501 | 1,112,000 |
| Steam | | 6.5000 | | 1200 | 188,302 | |
| Acceptor | (506.86) | | | 1856 | 220,691 | |
| MgO.CaO | 403.83 | 4.4692 | | | | |
| Inert | 76.03 | | | | | |
| Heat of Reaction | | | | | | |
| MgO.CaO to MgO.$CaCO_3$ | | | | | 119,192 | |
| | | | | | 542,686 | 1,112,000 |
| **Output** | | | | | | |
| Fuel Char to Regenerator(2) | 35.15 | | | 1500 | 16,659 | 332,170 |
| Reject Acceptor | (11.519) | (.08938) | | | 4,148 | |
| MgO.$CaCO_3$ | 5.572 | .03128 | 35.00 | | | |
| MgO.CaO | 4.392 | .05780 | 64.66 | | | |
| MgO.CaS | .034 | .00030 | .34 | | | |
| Inert | 1.521 | | | | | |
| Acceptor to Regenerator | (564.41) | (4.3798) | | | 203,264 | |
| MgO.$CaCO_3$ | 215.23 | 1.5329 | 35.00 | | | |
| MgO.CaO | 273.02 | 2.8322 | 64.66 | | | |
| MgO.CaS | 1.653 | .0147 | .34 | | | |
| Inert | 74.51 | | | | | |
| Product Gas, dry basis | | 7.1773 | | | 79,951 | 935,105 |
| $CH_4$ | | | 6.08 | | | |
| CO | | | 15.19 | | | |
| $CO_2$ | | | 6.91 | | | |
| $H_2$ | | | 70.91 | | | |
| $H_2S$ | | | .033 | | | |
| $NH_3$ | | | .65 | | | |
| $N_2$ | | | .22 | | | |
| Unconverted Steam | | 2.3620 | | | 75,407 | |
| Heat of Reaction | | | | | | |
| Ht. of Combustion (reactants - products ex Acceptor) | | | | | 155,275 | (-155,275) |
| Coal sulfur to MgO.CaS | | | | | 4,524 | |
| Heat Loss | | | | | 3,458 | |
| | | | | | 542,686 | 1,112,000 |

| | (1) | (2) |
|---|---|---|
| H, wt. % | 4.01 | .54 |
| C | 65.37 | 63.41 |
| N | 1.10 | .25 |
| O (diff.) | 17.17 | 2.26 |
| S | .90 | .97 |
| Ash | 11.45 | 32.57 |

* Lignite is fed to gasifier at 500°F and contains zero free moisture. Raw lignite contains 33.67% moisture, which is removed in dryer-preheater.

Consolidation Coal Co.
December 5, 1974

TABLE 2

$CO_2$ ACCEPTOR PROCESS (4)

Regenerator Heat and Material Balance
System Pressure, 150 psig

Basis: 100 lb dry lignite fed to gasifier

Datum: 60°F, liquid water

| | Lbs. | Mols | Mol % | °F | Enthalpy, BTU | Ht. of Combustion, BTU |
|---|---|---|---|---|---|---|
| **Input** | | | | | | |
| Fuel Char (1) | 35.15 | | | 1500 | 16,659 | 332,170 |
| Char Lift Gas (same composition as outlet gas) | | .440 | | 290 | 807 | 1,370 |
| Air | | 8.2973 | | 290 | 4,365 | |
| $O_2$ | | | 20.88 | | | |
| $N_2$ | | | 78.53 | | | |
| $H_2O$ | | .0490 | .59 | | | |
| Acceptor | (564.41) | (4.3798) | | 1500 | 203,264 | |
| $MgO.CaCO_3$ | 215.23 | 1.5329 | 35.00 | | | |
| MgO.CaO | 273.02 | 2.8322 | 64.66 | | | |
| MgO.CaS | 1.653 | .0147 | .34 | | | |
| Inert | 74.51 | | | | | |
| Makeup Stone | ( 18.003) | | | 60 | 0 | |
| $MgCO_3.CaCO_3$ | 16.482 | .08938 | | | | |
| Inert | 1.521 | | | | | |
| Heat of Reaction | | | | | | |
| Sulfide Sulfur (in - out) | | | | | 217 | |
| Heat of Combustion (reactants - products, ex acceptor) | | | | | 294,118 | ( -294,118) |
| | | | | | 529,430 | 39,422 |
| **Output** | | | | | | |
| Overhead Ash (2) | 12.547 | | | 1856 | 5,535 | 6,352 |
| Calcined Acceptor | (506.86) | | | | 220,691 | |
| MgO.CaO | 430.83 | 4.4692 | | | | |
| Inert | 76.03 | | | | | |
| Gas (3) | | 10.6765 | | | 173,405 | 33,070 |
| CO | | | 2.47 | | | |
| $CO_2$ | | | 32.06 | | | |
| $H_2$ | | | .056 | | | |
| $N_2$ | | | 64.07 | | | |
| $H_2O$ | | | 1.29 | | | |
| Heat of Reaction | | | | | | |
| $MgO.CaCO_3$ to MgO.CaO | | | | | 116,807 | |
| $MgCO_3.CaCO_3$ to MgO.CaO | | | | | 10,816 | |
| Heat Loss | | | | | 2,176 | |
| | | | | | 529,430 | 39,422 |

| | (1) | (2) |
|---|---|---|
| H, wt. % | .54 | - |
| C | 63.41 | 3.55 |
| N | .25 | - |
| O (diff.) | 2.26 | - |
| S | .97 | 5.19 |
| Ash | 32.57 | 91.26 |

(3) Gas also contains the following sulfur compounds, ppmv:

| | |
|---|---|
| $SO_2$ | 371 |
| $S_2$ | 6 |
| $H_2S$ | 37 |
| COS | 54 |

Consolidation Coal Co.
December 5, 1974

Table 3

STREAM IDENTIFICATION FOR FIGURE 3

| Stream | Identification | Flow Rate | Comments |
|---|---|---|---|
| 1 | Lignite feed | 2,296,500 lb/hr | Main lignite stream from mine. |
| *2 | Rain runoff | e.g. 6 in. in 24 hr. | Drainage from storage and coal prep'n. area. |
| *3 | Vent gas from dryer | 31.3 MM SCFH | Hot gas from drying and preheating. |
| *4 | Ash from dryer fuel | 9790 lb/hr | Fly ash from burning lignite fines. |
| *5 | Reject acceptor | 162,810 lb/hr | Removed to maintain activity of acceptor. |
| 6 | High pressure steam | 525,000 lb/hr | From waste heat boiler on raw gas. |
| 7 | Low pressure steam | 190,000 lb/hr | From waste heat boiler on raw gas. |
| 8 | Cooling water | 8,800 gpm | From cooler on water scrubber. |
| *9 | Warm air | 670 MM SCFH | From air fin cooler after scrubber. |
| 10 | Sour water | 612,000 lb/hr | From scrubber; contains $H_2S$, $NH_3$ (10,700 lb/hr), tar, phenols, etc. |
| *11 | Fine solids | not defined yet | From clarifier on scrubber. |
| 12 | Water condensate | 63,000 lb/hr | From steam reboiler (clean water). |
| *13 | Chemical purge | -- | e.g. amine, used for acid gas removal. |
| 14 | $H_2S/CO_2$ to Sulfur plant | 220,000 SCFH | $H_2S/CO_2$ removed and 5.9% $H_2S$ sent to sulfur plant. |
| 15 | High pressure steam | 1,050,000 lb/hr | From waste heat boilers recovering heat of reaction. |
| 16 | Water condensate | 483,000 lb/hr | Formed by methanation reaction. |
| 17 | Cooling water | 12,000 gpm | Cooling water on compressor. |
| 18 | Water | 3,700 lb/hr | Removed on compressor and dryer. |
| 19 | Rain | e.g. 6 in. in 24 hr. | Rain on coal storage pile. |
| 20 | Air | 14.3 MM SCFH | Combustion air on dryer-preheater |
| 21 | Solid fuel to dryer | 86,870 lb/hr | Lignite fines burned on dryer. |
| 22 | Gas fuel | 1.00 MM SCFH | Gas fuel to preheater and dryer. |
| 23 | Steam | 1,653,700 lb/hr | Reaction steam to gasifier. |
| 24 | Boiler feed water | 525,000 lb/hr | To waste heat boiler. |
| 25 | Boiler feed water | 190,000 lb/hr | To waste heat boiler. |
| 26 | Air for cooling | 670 MM SCFH | Air to air-fins on raw gas. |
| 27 | Cooling water | 8,800 gpm | Cooling water on raw gas. |
| 28 | Steam for heating | 63,000 lb/hr | For reboiler or regeneration. |
| 29 | Amine or scrubber medium | -- | Scrubbing liquid on acid gas removal. |
| 30 | Boiler feed water | 1,050,000 lb/hr | Steam generator on methanator. |
| 31 | Cooling water | 12,000 gpm circl. | For after cooler on compressor. |
| 32 | Dryer agent | -- | Glycol, molecular sieve, or other drying agent. |
| 33 | Steam from regenerator heat recovery | 567,000 lb/hr | Steam generated (excludes superheating). |
| *34 | Flue gas from turbine | 57.3 MM SCFH | Dust control provided - after turbine. |
| *35 | Dust | unknown | From dust removal - after turbine. |
| *36 | Sulfur | 9,920 lb/hr | From Sulfur plant. |
| *37 | Flue Gas | 960,000 SCFH | Tail gas from sulfur plant. |
| 38 | Steam | 6,300 lb/hr | Generated by sulfur plant. |
| 39 | Cooling water | 42,900 gpm circl. | From cooling tower. |
| *40 | Air | 620 MM SCFH | Used for cooling (plus 535,000 lb/hr water evap.) |
| *41 | Water | 43,000 lb/hr | Drift loss. |
| 42 | Additives | -- | e.g. chromium, chlorine, used to control fouling and corrosion. |
| 43 | Air | 44.5 MM SCFH | Combustion air to regenerator. |
| 44 | Dolomite | 254,454 lb/hr | Make-up acceptor. |
| 45 | Boiler feed water | 567,000 lb/hr | To waste heat boiler on regenerator gas. |
| 46 | Fuel gas | 65,000 SCFH | To incinerator on Claus plant. |
| 47 | $H_2S/CO_2$ Streams | 670,000 SCFH | Streams 14 and 53. |
| 48 | Air | 337,000 SCFH | For oxidation in Claus reaction. |
| 49 | Boiler feed water | 6,300 lb/hr | To waste heat boiler on Claus plant. |
| 50 | Cooling water | 42,900 gpm circl. | Warm cooling water in |
| 51 | Air | 620 MM SCFH | ambient air to cooling tower. |
| 52 | Additives | -- | e.g. chromium, chlorine, used to control fouling and corrosion. |
| 53 | $H_2S/CO_2$ | 450,000 SCFH | Stripped off in ash desulfurization. |
| *54 | Ash slurry | 466,000 lb/hr | Carbonated ash from ash desulfurizer in 50% slurry with water. |
| *55 | Ammonia | 11,200 lb/hr | By-product recovered from waste water tr. |
| *56 | Oil, phenols | unknown | Separated from waste water treat. |
| *57 | Sludge | -- | Separated from waste water treat. |
| 58 | Water | 1,420,000 lb/hr | Treated make-up water. |
| *59 | Sludge | -- | From make-up water treatment. |
| *60 | Miscellaneous chemicals | -- | $H_2SO_4$, caustic, alum used for treating. |
| 61 | $CO_2$ | 600,000 SCFH | Stripping gas to ash desulfurization. |
| 62 | Water | 15,800 lb/hr | Used in ash desulfurization. |
| 63 | Sour Water | 612,000 lb/hr | From scrubbing raw gas. |
| 64 | Water | e.g. 6" in 24 hr. | Rain run-off from coal storage and process areas. |
| 65 | Miscellaneous chemicals | -- | If used to treat waste water. |
| 66 | Water | 1,420,000 lb/hr | Make-up water to plant. |
| 67 | Miscellaneous chemicals | -- | As used to treat make-up water. |

* NOTE: These streams are emitted to the environment.
All others are retained within the process.

oxides is just enough to use up all of the hydrogen during methanation. The latter gives a very high heat release corresponding to 19% of the heating value on the gas fed to methanation. It is highly desirable to recover this heat in the form of steam or useful preheat, as otherwise it must be rejected to cooling water or air.

The regenerator serves two purposes in that it calcines the acceptor to remove $CO_2$, and in addition reheats the acceptor to supply sensible heat to the gasification reactor. Regenerator fuel is supplied by feeding a separate stream of char from the gasifier, and burning it completely in the regenerator. Thus, the dolomite is separated from char by elutriation in the reactor before it is circulated to the regenerator. The regenerator is operated under slightly reducing conditions in order to avoid sulfate formation which causes fusion and deposits. The flue gas contains 2.47 Vol. % CO, and this is burned to generate additional heat for recovery. The hot flue gas goes through a heat exchanger to superheat steam to 1200°F. The hot flue gas is then used to generate additional steam in a boiler before passing to the flue gas turbine. The turbine generates enough power to drive both the air compressor and the product gas compressor.

As a result of the favorable energy balance for the acceptor process, no utility boiler is required to supply steam or power for the process during normal operation. In other words, all utilities are provided by waste heat recovery to generate steam, together with the output of the flue gas turbine. No oxygen is needed but there will be a sulfur plant, and waste water treatment to control phenols, ammonia, and suspended solids. The only water effluent from the plant in normal operation will be the water used to slurry residual ash from the lignite feed. Some spent acceptor is rejected to maintain activity and this will be in a dry form, low in sulfur, and probably is suitable to use as land fill. It appears that surplus power or steam could be made available from the process as shown, and supplied to the shops, mine, and general off sites. A more extensive utilities study would be needed to explore this.

Ash from the regenerator has a high sulfur content in forms such as calcium sulfide which could cause a secondary pollution problem due to release of hydrogen sulfide. The developer, therefore, included treatment of the ash with carbon dioxide and water at 190°F to remove 98% of the sulfur. The resulting $H_2S$ is sent to the sulfur plant. Flow rates for the ash desulfurizing operation are shown in Figure 2 based on 25% excess $CO_2$ over the theoretical. It may be assumed that the $CO_2$ required in the ash desulfurizer will be supplied from the regenerator flue gas, 3% of which could supply all the $CO_2$ needed. The flue gas might be used directly, or it might be processed to provide a more concentrated stream of $CO_2$.

## 1.2 Effluents to Air in Main Gasification Stream

Effluents to the air are shown in Figure 4 and listed in Table 3 for the case incorporating modifications to improve environmental aspects, and to include all auxiliary facilities and utilities. The plant is sized to make 250 x $10^9$ Btu/day of synthetic natural gas having a higher heating value of 952 Btu per cubic foot (262.6 MM SCFD). Total consumption of lignite is 28,517 tpd of 33.67% moisture content. The preheated lignite fed to the gasifier contains .90% sulfur, 11.45% ash, and has a higher heating value of 11,120 Btu per pound. Further details on the feed and products are given in Tables 1 and 2 and in Reference 3.

### 1.2.1 Coal Preparation

The first effluent to the air in the process flow is from the coal storage and preparation area. Large storage piles are needed in view of the high lignite consumption rate, and dust problems can be expected due to wind, handling, loading, and unloading. The equipment should be completely enclosed as much as possible to minimize dusting and spills. Precautions are also needed to prevent fires in the storage pile, as lignite is especially liable to spontaneous combustion (5). Tamping down of the storage pile as it is being formed is one customary precaution, but facilities and plans are also needed for extinguishing fires if they occur. These are general observations and need careful consideration and definition for specific projects.

The next effluent is from the coal drying system where hot combustion gas is contacted with the lignite feed containing moisture to accomplish drying. General requirements are that the hot gas must be introduced at less than 1000°F so that local over-heating does not occur and release a large amount of volatile material from the lignite. Also, oxygen content of the gas is held down to about 11% or less by recycling flue gas, in order to meet safety requirements.

Coal drying and preheating is a major area for consideration, due to the large fuel consumption (8-9% of the lignite feed) and the large volume of vent gas (1156 MM cfd) to be cleaned of dust and sulfur. The original design used only lignite fines for fuel and has a high sulfur emission, 1.6 lbs of $SO_2$ per MM Btu fired vs 1.2 lb/MM Btu allowed for large stationary power generation. Therefore, a modified design was made with supplemental fuel gas to reduce total sulfur emission. These cases are discussed in sub-sections below.

For large coal fired stationary power plants, $NO_x$ content of the flue gas must meet the emission standard of 0.7 lb $NO_2$/MM Btu. It has been shown that $NO_x$ can be decreased by minimizing excess air, and by designing the combustion system to limit flame temperature. These same considerations should be incorporated in coal fired operations used to dry and preheat coal.

1.2.1.1 Original Design

A flow plan of the overall coal preparation system supplied by the developer is shown in Figure 1, and corresponding flow rates are shown in Figure 5. Raw lignite containing 33.67% moisture is fed to a grinder which is swept with hot recirculating gas to dry the lignite down to 16% moisture. Part of this is further heated to 500°F in the preheater to provide feed to the gasifier, while the remainder is used as fuel in the three furnaces of the coal preheat section. One of these furnaces supplies hot gas to the grinder, another to the dryer, and the third to the preheater. In each case, hot gas from the furnace is tempered with recirculating flue gas or with flue gas from the regeneration vessel so as to avoid local overheating of the lignite, which would release volatile combustible matter.

Combustion of the lignite fuels generate ash which needs to be separated and rejected. Slagging type furnaces are used, where an estimated 70% of the ash is removed. Hot gas leaving the furnace is tempered and passed through cyclones to remove nearly all of the remaining ash. If the final ash content of the hot gas is comparable to the 0.1 lbs per MM Btu required on stationary boilers, then overall separation of the ash must be 99% efficient. This degree of separation has been difficult to achieve with conventional cyclones in power plant boilers using coal fuel.

The hot gas is contacted with lignite in the grinder and will pick up lignite fines which also need to be recovered. To meet the comparable dust loading for stationary boilers of 0.1 lbs per MM Btu, the dust remaining in the vent gas after final clean-up can be only 155 lbs per hour. That this represents a difficult clean-up problem is illustrated by the fact that the loss corresponds to only .01 weight percent of the lignite charge on a dry basis. Emission of dust might be controlled adequately by using bag filters, electrostatic precipitation or a scrubber. Recovered solids could be returned to the gasifier or regenerator vessel, while ash from the furnaces can be disposed of along with the carbonated ash from the ash desulfurizer.

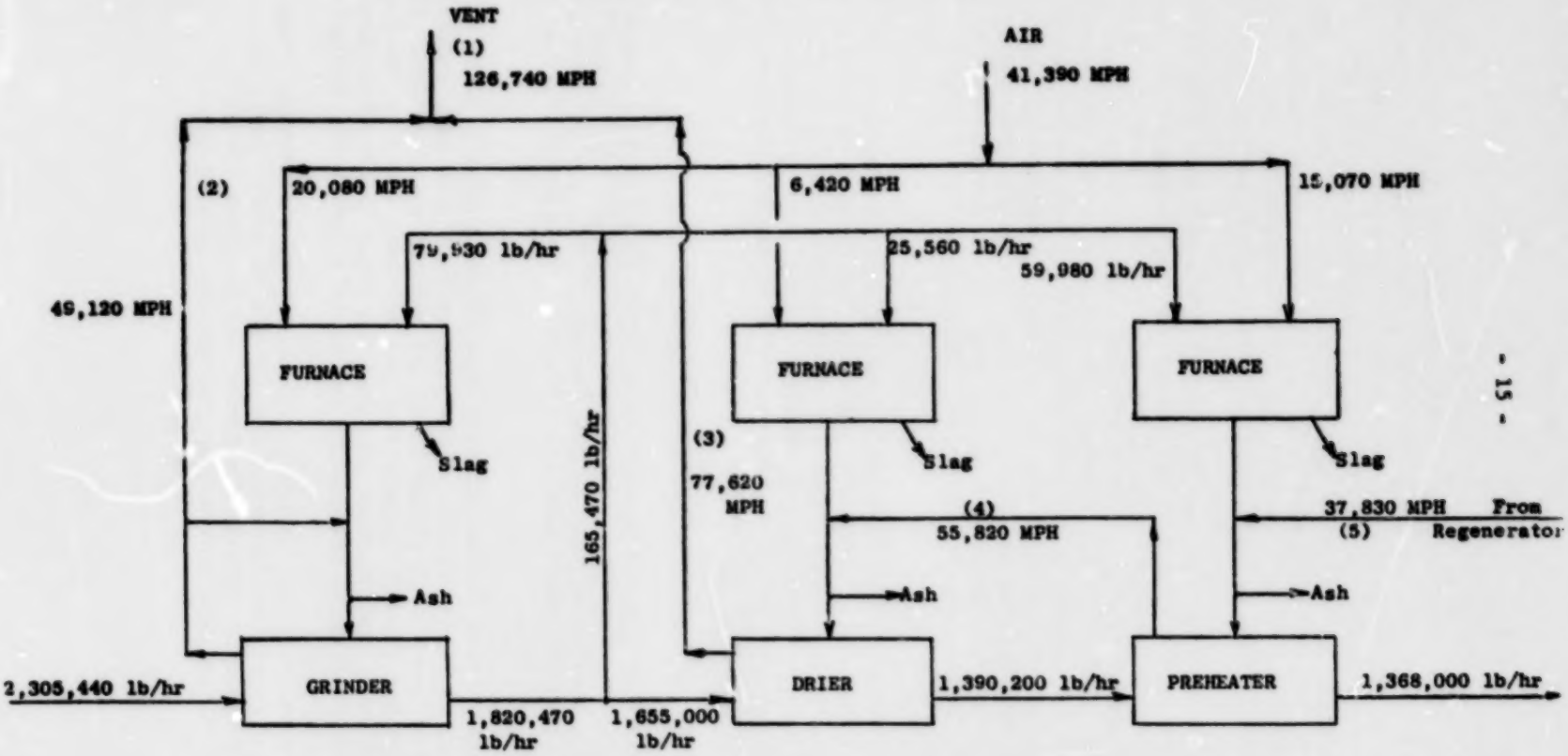
Sulfur content of this particular lignite is such that when it is used as fuel, the sulfur content of the resulting flue gas will exceed the specification set for stationary boilers. It gives 1.6 lbs of $SO_2$ per million Btu vs the 1.2 specification. The developer has pointed out that the lignite is adsorbent and may remove sulfur compounds from the flue gas. If 25% of the sulfur were adsorbed in this way then the flue gas would meet emission standards for stationary boilers. This would be very desirable and screening experiments should be made to explore the possibility. Stack gas clean-up could also be used in order to reduce the sulfur emission to a reasonable level. Processes are offered commercially for this, such as limestone scrubbing or one of the regenerable liquid scrubbing systems.

One further concern on emissions from the coal preparation area is with regard to odors. Lignite is a relatively reactive material and when dried and preheated to 500°F small amounts of vapors are evolved including carbon dioxide and combined water.

Figure 5

CONSOL FLOW DIAGRAM FOR LIGNITE GRINDING AND DRYING

Basis: 250 x $10^9$ MM Btu/Day of Pipeline Gas




| Stream | (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|---|
| $O_2$, mol % | .40 | .77 | .16 | 0 | .12 |
| $CO_2$ | 15.67 | 7.16 | 21.06 | 27.77 | 32.76 |
| $H_2O$ | 38.48 | 59.91 | 24.92 | 6.88 | 1.28 |
| $SO_2$ | .0438 | .0379 | .0476 | .0555 | .0449 |
| $N_2$ | 45.40 | 32.11 | 53.81 | 65.79 | 65.79 |

It is also possible that undesirable odors will be released, particularly if there are any zones of local overheating. If odors are a problem then it may be necessary to provide incineration on the effluent gas. This would, of course increase the fuel requirement quite significantly, so hopefully it can be avoided. If the odors are only associated with the preheater offgas, then this stream could be sent to the combustion zone of one of the other furnaces for incineration. Since it is a small stream, there would be little effect on heat balances.

Emission of nitrogen oxides from the furnaces must also be controlled. The usual techniques for decreasing $NO_x$ formation are generally aimed at lowering the combustion or flame temperature. Since the furnaces in this design operate with a high combustion temperature to produce slagging, it is likely that the emission of nitrogen oxides will exceed the standard of 0.7 lbs $NO_2$ per MM Btu specified for stationary power plants. One method of control would be to lower the combustion zone temperature in the furnaces by adding inert gas available from the regeneration system, or flue gas from the coal drying system could be recycled to the furnace for this purpose. More ash would then be removed by the cyclones.

There is an urgent need for effective practical methods to remove $NO_x$ from flue gas. Although no established process is available now for this purpose, a considerable effort is being directed at the problem in the United States and elsewhere. Progress is encouraging, and it is expected that suitable processes will be demonstrated and become available in the near future.

1.2.1.2 Revision to Decrease Sulfur Emission

In the modified design, sulfur emission from the coal preparation section is decreased primarily by using some desulfurized low Btu gas from the gasification section as fuel to the furnaces. This gas is not methanated but rather is drawn off after acid gas removal. The modified system is shown in Figure 6.

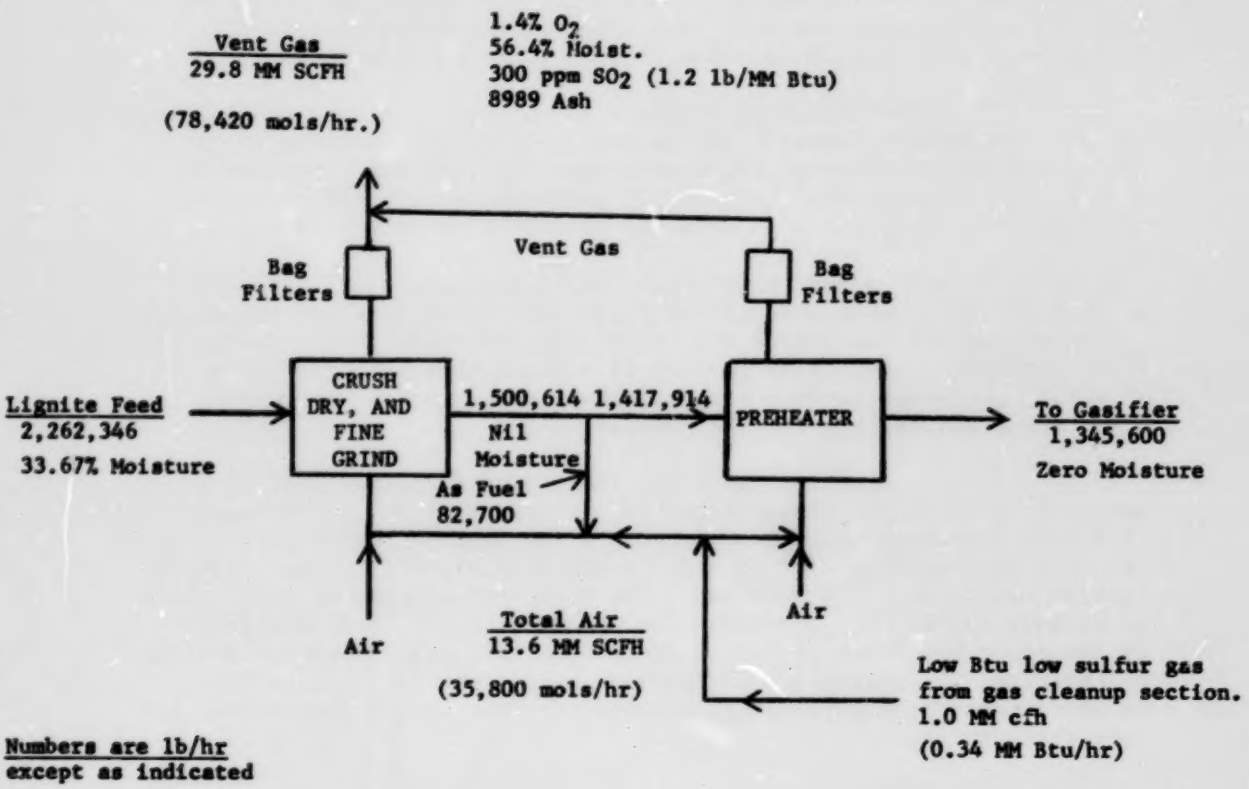
To bring total sulfur emission down to the target 1.2 lbs $SO_2$ per MM Btu requires replacing 25% of the lignite fuel with gas, corresponding to 1.0 MM SCFH or about 2.6% of the total gas made by gasification. For simplicity, flue gas from the regenerator has not been added to the coal preparation system. Instead, flue gas from the dryer is recycled through the furnaces to lower flame temperature and thereby reduce $NO_x$ formation.

As in the original design, cyclones are used to separate ash from the hot gas after the furnace. The hot gas of course picks up lignite fines in passing through the drying and grinding operation, therefore, bag filters are provided on the vent gas streams in order to recover all dust.

Figure 6

COAL DRYING SYSTEM

ALTERNATIVE TO DECREASE SULFUR EMISSION




Numbers are lb/hr
except as indicated

Separate bag filters are provided on the preheater. This operation consumes only 12% of the total fuel for coal preparation, and only gas fuel is fired to it. Consequently, all of the fines recovered from the gas leaving the preheater are pure lignite and can be used as fuel for the furnaces if desired.

To minimize loss of fines in the dryer, it can be operated on a relatively coarse crushed lignite of say 1/2" size. Then the fine grinding can be carried out after the dryer and before the preheater. With this arrangement the very fine lignite is exposed to a smaller volume of gas so that the problem of dust recovery is minimized.

The modification to decrease sulfur emission does not increase the air requirement compared to the original design. Neither is the fuel consumption increased for coal preparation, or the total amount of raw lignite consumed. Feed to the gasifier is 2.6% higher, since more gas must be produced in order to provide some clean gas fuel.

In applications where water is in short supply, it should be possible to recover make-up water from the dryer vent gas by passing it through an air fin cooler and collecting the condensate. Total water content is about 1500 gpm and if most of this were recovered it would be a large contribution relative to the net make-up water requirement of 2786 gpm for the process.

In any situation where gas fuel is used for heating, it is possible to use conventional technology to generate by-product electricity in a turbine-generator. This applies to the modified dryer design, where the fuel gas could be used to drive a gas turbine, and hot gas from the turbine would go to the furnaces. The potential by-product power would be roughly 20,000 KW. Increased fuel consumption directly chargable to the power would correspond to about 80% efficiency on conversion to electricity. In general, this approach merits careful consideration in situations where substantial amounts of clean gas or liquid fuel are used for heating.

### 1.2.2 Gasifier

No gas streams are released directly to the atmosphere from the gasifier, but a stream of spent acceptor solids is removed essentially free of char, the separation having been made within the gasifier. This reject acceptor could result in a dust nuisance which needs to be controlled by water sprays and careful handling. It leaves the gasifier at 1500°F and although the method for cooling is not shown, a fluid bed cooler would seem to be preferred to allow generating steam for use in the gasifier. Final cooling might be by dropping into water but this would add a problem on water clean-up. Therefore, we have used a small amount of water that is evaporated to dryness so that the material

is not wetted. Steam from final cooling can be collected and sent to the bag filter system. Based on pilot plant experience it is expected that the reject acceptor will be suitable for land fill without further treatment, and additional tests on leaching, sulfur release, etc. are needed to be sure of this.

### 1.2.3 Gas Cleaning

Raw gas leaves the gasifier through cyclones which remove most of the solids. It is cooled in a waste heat boiler to make steam, and then scrubbed with water to remove essentially all of the dust using Venturi type scrubbers operating at the dew point and evaporating a small amount of water. The gas is further cooled to 150°F in air-fins so as recover condensate and conserve cooling water.

### 1.2.4 Acid Gas Removal

The raw gas contains 330 ppm of sulfur, mainly as $H_2S$. Sulfur removal is required before methanating, but it is undesirable to remove much $CO_2$ because it is needed to consume the available hydrogen during methanation. Various processes have been reported that remove concentrated streams of $H_2S$ while allowing most of the $CO_2$ to pass through the absorber system (6,7,8). A major problem in most gasification systems is obtaining a $CO_2$ stream free from sulfur that can be vented. In the present case the sulfur only has to be removed to a level sufficiently low to prevent overloading the zinc oxide guard boxes.

Consideration should be given to using an absorption/oxidation process, such as Stretford, Takahax, IFP etc., on the raw gas directly. This would remove $H_2S$ only and convert it to sulfur product without removing $CO_2$.

As an alternative, it may be possible to take low sulfur ash from the ash desulfurizing system and add it to the scrubber water so as to pick up sulfur. Sulfur-containing ash could then be returned to the ash desulfurizing system for regeneration.

### 1.2.5 Methanation and Compression

Final clean-up of the gas is accomplished in a bed of zinc oxide before methanation, to remove traces of sulfur and dust which could foul the catalyst. There may be traces of tar fog, naphthalene, etc. present in the gas, in which case it would be desirable to include a guard bed of activated carbon. Methanation itself generates no effluents to the air. After methanation the gas is compressed to 1000 psig and dried, for example with glycol, before being sent to the pipeline.

### 1.2.6 Regenerator

The circulating dolomite is calcined at 1850°F to remove $CO_2$. Make up dolomite is also added and calcined. Heat is supplied by burning the required amount of char with air in a fluid bed regenerator operating at 150 psig. A small content of carbon monoxide is maintained in the outlet gas in order to avoid forming oxidation compounds of calcium which were found to cause deposits. The flue gas is removed through cyclone separators to take out most of the dust, consisting of ash residue from all of the lignite fed to the gasifier. This ash is removed from the system by way of a fluid bed cooler, and sent to the ash desulfurizing unit.

Gas from the cyclones passes to heat exchangers where steam is super-heated to 1200°F. Additional steam is then generated in a waste heat boiler. At an appropriate point in this system additional air can be added to burn up residual carbon monoxide (e.g. before the waste heat boiler). This is necessary to avoid releasing carbon monoxide to the atmosphere, and at the same time it provides a convenient way to recover high level heat by burning the carbon monoxide. It is known that this reaction is reasonably fast at temperatures above 1300°F. The reaction raises the gas temperature by about 300°F, which still leaves it lower than the regenerator temperature of 1850°F, consequently, deposits should not be a problem.

Flue gas then goes to an expansion turbine to recover power. For a turbine inlet temperature of 1000°F or higher, enough power can be generated to drive both the air compressor and the product gas compressor. In fact, there may be excess power available. Noise control for this area needs careful attention in a final plant design.

The flue gas contains 470 ppm of total sulfur, and can be discharged to the atmosphere, assuming that the dust content, nitrogen oxides, and odor are acceptable. Further information is needed on these critical items. The $NO_x$ content may be low, in view of the relatively low combustion temperature in the regenerator, but specific data should be obtained on this in the pilot operations. For treating the ash to remove sulfur, a stream of $CO_2$ is needed, which might be provided by scrubbing part of the flue gas.

### 1.2.7 Ash Desulfurizer

Ash produced from the coal is processed to give 98% sulfur removal by reacting it in a water slurry with $CO_2$ at 190°F. Off-gas containing a calculated 27% $H_2S$, 7% $CO_2$ and 66% $H_2O$ is sent to a sulfur recovery plant such as a Claus, Stretford, or other type unit. All of the gas streams in this system are contained and should not cause environmental problems. The carbonated ash is withdrawn as a 50% slurry in water and is not expected to create odors, although this should be checked out. $CO_2$ required for this operation is 1530 moles/hr, including 25% excess over theoretical and can be provided from the regenerator flue gas.

## 1.3 Effluents To Air - Auxiliary Facilities

In addition to the basic process, auxiliary facilities are required which will now be discussed with regard to effluents to the air.

### 1.3.1 Sulfur Plant

$H_2S$ streams from acid gas removal and from the ash desulfurizer go to a sulfur recovery plant. If a Claus plant is used, sulfur recovery of about 97% can be achieved with three stages in "straight-through" flow. The tail gas still contains about 3 tons per day of sulfur and might be cleaned up, although this gas volume of 20 MM cfd is small relative to the other effluents. In fact, in this process as opposed to others, the sulfur in the Claus tail gas represents such a small percentage of emitted sulfur (see Section 2) that investments or costs for sulfur removal could best be spent cleaning the regenerator flue gas or dryer vent gas. Thus, the Claus tail gas could be incinerated and vented to the dryer stack and a small additional quantity of clean product gas added as fuel to decrease total sulfur emissions to acceptable levels. No specific preference is indicated for sulfur recovery.

### 1.3.2 Utilities

Net utility requirements are low because considerable power is recovered by passing the regeneration flue gas through an expander turbine. Also a large amount of heat is recovered in waste heat boilers to generate steam, and on the methanator where the heat released by reaction amounts to about 19% of the heating value in the entering gas. Most of this can be converted to steam by recirculating gas from the reactor through waste heat boilers. Under development are alternative techniques using a fluid bed or liquid slurry reactor that should be more efficient.

A utilities balance for the process indicates that the process is self-sufficient in steam and power, so that no utility boiler is required for normal operation. It is likely that a more definitive and optimized utility balance will show that it is possible to make more steam and power than consumed by the gasification plant, so that these could be used for shops, mining operations, offices and general off-sites. For example, 1.65 million pounds per hour of steam at 150 psig is used in the gasifier. This could be generated at a higher pressure such as 600 psig and run through bleeder turbines down to 150 psig, while generating by-product power at the rate of about 40,000 kw.

In the utilities area, the main cooling tower has by far the largest volume of discharge. It is, therefore, critical from the standpoint of pollution. In this particular case it is not expected to contain significant amounts of undesirable contaminants. The cooling water circuit is clean and should not contain ash or objectionable materials such as phenols, oil, or $H_2S$. Normally a certain amount of leakage can be expected on exchangers using cooling water. Since the process operates mainly at 150 psig pressure, this should not be a major item. Also, most of the cooling water is from steam condensers on drivers rather than on oil, sour water, etc.

Total cooling water requirement is modest considering the plant size. Effluents to the air from this cooling tower amount to 457,000 lbs/hr of water evaporated, plus 43,000 lbs/hr of estimated drift loss or mist. Flow of air through the tower is 15,000 MM cfd.

The drift loss or mist will contain dissolved solids which can result in deposits on the ground and on nearby equipment, and in some cases drift loss has caused icing problems on equipment and public roads in the winter. With any cooling tower, the problem of fog formation must be assessed, since under certain conditions the moisture condenses and the resulting plume can be a problem if it affects public highways. Reheat of the stack gas is one way to reduce fog formation, but is inefficient. In planning the layout of the plant facilities, these aspects should be given careful consideration, and every effort made to avoid potential problems by proper placement of the equipment.

There will also be evaporation and the possibility of odor from ponds and water treating facilities. While most of the ammonia will be recovered as a by-product, the waste water still will contain traces of ammonia and probably also some phenols, hydrocarbons etc. particularly during start-up or during upsets. These must be controlled and a biological oxidation (biox) pond for waste water treating is needed. Depending upon pilot plant results with regard to tar and hydrocarbons produced, it may be necessary to provide an oil separator ahead of the biox unit, and possibly a froth floation separator. If these are required they should be covered to contain vapors and odors.

In addition, leaks on processing equipment can be expected. For example, packing on valves and seals on rotating equipment such as compressors and rotary dryers are commonly found to leak, depending upon operating pressure, design, and maintenance. Estimates must be made for specific projects to determine the magnitude and controls needed, as has been done for example on oil refineries in California (9).

## 1.4 Liquids and Solids Effluents

### 1.4.1 Coal Preparation

Coal storage and preparation is the first major item in this category. The problem is due to rain runoff. The storage pile has a very large volume such as 30 days holdup and the residence time is long so that rain has a chance to react and form acids or extract organics, sulfur, and soluble metals, and in any event give suspended matter in the rain runoff. Therefore, it is necessary to collect water from this area as well as from the process area, and send it to a separate retention pond. This pond should have a long enough residence time for solids to settle out; also, there will be a certain amount of biological action which will be effective in reducing contaminants. Limestone can be added in this circuit if needed to correct acidity. The problem may bear some resemblance to acid mine water and should be reviewed from that standpoint (10). Rain from the dolomite storage area should also be included.

In some comparable situations, seepage down through a process area can be a problem in addition to the runoff. Even though storm sewers collect the runoff in a chemical plant or refinery, leaks and oil spills can release enough material such that it actually seeps down into the ground water supply. If the ground contains a lot of clay this will not normally be a problem - in fact the clay can absorb large quantities of metallic ions. In sandy soil it may be necessary to provide a barrier layer underneath the coal storage piles. This could be concrete, plastic or possibly a clay layer. Storm sewers from the process area should also be collected and sent to the pond. In the present design this should be satisfactory. However, in other cases where there can be serious spills of oil and phenols, the process area should be drained to a separate holding pond.

Water from the retention pond will be relatively clean and low in dissolved solids and is therefore a good make-up water for the cooling tower circuit and for preparation of boiler feed water. Normally all of the run-off water can be used in this way so that it will not constitute an effluent from the plant.

No specific solid or liquid effluents are expected from the coal or dolomite grinding, drying, and preheating sections, except that dryer vent gas will be passed through bag filters to recover the dust consisting of ash from burning lignite fines. It can be combined with the ash slurry and returned to the mine. Electrostatic precipitators or scrubbers may be used instead of bag filters.

As mentioned earlier,scrubbing of the dryer vent gas may be used to reduce sulfur emission. If so, then all water and solids from this operation should be returned to the process, for example, to the gasification section so that they are not allowed to become an effluent from the plant.

### 1.4.2 Gasifier

The only discharge stream from the gasifier is the reject acceptor which is replaced at the rate of 2% per day of circulation in order to maintain activity. The acceptor is relatively coarse compared to the char in the gasifier, and is separated from it before being removed. Since the reject acceptor is coarse it probably will not be a dusting problem but water sprays may be used if required to control this.

The reject acceptor is stated to be low in sulfur, 0.084%, which is low enough so that there should be no secondary pollution problem upon its disposal. It would appear to be a suitable material for land fill and should be considered for such use.

### 1.4.3 Gas Clean-Up

Raw gas leaves the gasifier by way of cyclone separators which remove most of the dust. The gas is cooled as discussed in Section 1.2.3, and a water scrubber removes residual dust and ammonia. The scrubber water will also contain sulfur compounds, since the gas contains 330 ppm $H_2S$. Unreacted steam from the gasifier is condensed in this system, constituting an effluent which must be treated and disposed of or reused. Amounts of the various streams are shown on Figure 3 and in Table 3.

Water from scrubbing goes first to a clarifier which removes fine solids. It is expected that the amount of solids will be small and can be disposed of along with the spent ash being returned to the mine, otherwise they may have to be used in the process or burned as fuel, depending on combustible content. Further information is required on the nature of this stream. Clarifier water goes to a sour water stripper, to separate ammonia and $H_2S$. If ammonia can be sold as a by-product, purification facilities can be included, using designs that are available, to produce 130 tpd.

Effluent from the sour water stripper will also contain traces of phenols, tar, naphthalene, etc. which must be cleaned up. For this purpose we have added a biox unit and retention pond to reduce the contaminants to a low enough level so that the water can be recycled as make-up water. Detailed information for designing this system should be obtained by the developer when representative streams become available from pilot plant operations to show whether the assumed clean-up system is adequate. If not, it may be necessary to include such things as oil separators and activated carbon adsorption. This stream should not be allowed to become an effluent from the plant.

The next area is acid gas removal, where the main requirement is to remove sulfur compounds prior to methanation. A small amount of $CO_2$ may also be removed but this is incidental and the process depends on leaving nearly all of the $CO_2$ in the gas going to methanation in order to consume the large amount of hydrogen available. The $CO_2$ content is 6.9 Volume % and it would be acceptable to remove up to 10% of it. Acid gas removal presents somewhat of a problem in that the usual scrubbing systems remove much of the $CO_2$ when operated for high sulfur removal. Some of the higher amines are more selective for removing $H_2S$ but may not be sufficiently so.

A possible alternative is to use the carbonated ash produced by the ash desulfurizing unit to remove sulfur compounds from the gas. This would need to be tested experimentally but if it works it may be possible to simply add desulfurized carbonated ash to the water scrubbing system and remove most of the sulfur at that point. The ash would then be returned to the ash desulfurizing system for regeneration and sulfur removal. The total amount of sulfur in the gas is only 12 tpd, so there may be simplier ways to remove it than by using conventional acid gas scrubbing. Caustic wash, for example, is one possible route.

The final gas clean-up needed to protect the methanation catalyst is accomplished by passing the gas over zinc oxide at elevated temperature, about 600°F, to remove traces of various sulfur compounds. The zinc oxide charge is replaced when it is spent, being returned to a manufacturer for processing.

There is a distinct possibility that small amounts of certain elements such as fluorine, chlorine, bromine, arsenic, etc. will volatilize in the gasifier in the presence of steam and hydrogen, as is experienced in oil refining and other operations. In addition, nickel and iron may form carbonyls by reaction with CO. Experimental work is needed in this area to identify the problem so that it can be taken into account and control measures taken if required.

### 1.4.4 Methanator

Methanation increases the heating value of the gas up to pipeline quality by reacting the carbon oxides with hydrogen present in the gas to form methane and water. Feed gas composition is such

that the reaction goes to completion with only a few percent of hydrogen remaining. The methanation reactor may use a fixed bed of nickel catalyst, or the spray coated catalytic tubes used by the Bureau of Mines, or one of the other processes under development. The latter include a fluid bed system with cooling coils in the bed, and an alternative using a liquid slurry of catalyst.

The methanation reaction operates at about 800°F, and releases considerable heat which must be removed to prevent excessive temperatures. In the fixed bed system this is usually accomplished by dividing the reactor up into a number of catalyst beds in series, with gas recirculation through coolers on the various beds. Heat release amounts to about 19% of the heating value of the entering gas, resulting in a considerable loss in thermal efficiency. However, if the heat is mostly recovered to make useful high pressure steam the debit is greatly reduced. A further characteristic of the methanation reaction is that it produces a considerable amount of water, 483,000 lb/hr in this design, compared to the 1,650,000 lb/hr injected into the gasifier reactor. This water is a very clean condensate - thus the methanator makes a large contribution in the overall water balance. The methanation catalyst will eventually be replaced when it has lost activity, and the spent catalyst should be returned to the manufacturer for metals recovery or reprocessing.

### 1.4.5 Gas Compression

The final step is to compress the methanated gas from about 140 psig to pipeline pressure of 1,000 psig, and dry it. Compression normally involves inter coolers and after coolers from which condensed water will be removed - again, it is high quality condensate. The gas then passes through a clean-up dryer, such as one using glycol, alumina, or molecular sieves, in order to meet pipeline specifications of 7 lbs of water per million cubic feet. Product gas is of pipeline quality, with a heating value of 952 Btu per cubic foot.

Gas compression requires about 33,000 brake horse power, which can be supplied from the flue gas expander turbine. As an alternative, the compressor could use steam drivers, but the flue gas turbine allows large savings in steam and cooling water requirements.

### 1.4.6 Regenerator

The regenerator serves to calcine the acceptor for recirculation and also supplies heat to the system. There are no liquid or solid effluents from the regenerator, except an ash stream which is carried overhead to cyclones and must be separated efficiently from the gas before it goes to the flue gas turbine. Details of the system for removing this dust and the efficiency of removal were not specified, but it is indicated that high pressure drop cyclones will be used.

A reliable and efficient system for removing dust from the regenerator flue gas is required.

Federal regulations for large stationary boilers limit the emission of particulates to 0.1 lb/MM btu, corresponding to about 400 lbs/hr of solids for the present design. This would require a dust removal efficiency of 99.7%, which would correspond for example to an efficient electrostatic precipitator. The allowable solids will also be limited by erosion in the flue gas turbine which may call for an even lower level. (18)

One manufacturer has specified a maximum dust loading of 30 ppm by weight in gas fuel for turbines, with a maximum particle size of 10 microns. Other specifications require less than 20 ppm of solid and a maximum particle size of 2 microns, in connection with public utility applications. These present very difficult targets for dust removal, particularly since it is desired to remove the dust at 1000°F or higher. The use of several stages of cyclones has been indicated for this service, with the final clean-up by means of high pressure drops cyclones. In the case of cyclones offered by some manufacturers, increased centrifugal force, and higher recovery, is obtained by tangentially injecting an extraneous stream of clean gas at high velocity into the cyclone. Sand bed filters have also been proposed for this service. In general, this area of dust removal at high temperature represents a very important technological need, where additional work could lead to a major contribution in improving the environmental aspects of energy conversion.

While dust removal has been discussed from the standpoint of erosion on the flue gas turbine, there are indications that corrosion can be at least as important as erosion in setting limitations. Sulfur is, of course, a major concern as well as alkali metals such as sodium, calcium, etc. One specification sets a maximum of 5 ppm, calculated as alkali metal sulfates, which are especially corrosive. Most of the work being done in this area is with turbines in oxidizing atmospheres containing a high percentage of oxygen. In the present design, the turbine operates in an atmosphere containing little or no free oxygen, which may aggravate corrosion. However, secondary air could be added ahead of the turbine in order to increase the free oxygen content, with a corresponding change in flow rates for the system.

The incentive for using a flue gas turbine to recover energy from hot regenerator flue gas in the $CO_2$ Acceptor process is very great. This is also the case for similar situations where hot dusty gas is available at high pressure and must be depressured, as on catalytic cracking units in oil refineries, where some commercial units are already in use (17). Therefore the intensive effort now directed at broader application of gas turbines is well warranted, and can be expected to result in major contributions.

If the turbine is capable of handling high dust loadings then it may be necessary to add dust recovery after the turbine. In this case, electrostatic precipitation, water scrubbing, or bag filters could be used. If water scrubbing is used it may be possible to remove additional sulfur at the same time by adding spent ash or rejected acceptor to the scrubbing water. Every effort should be made to incorporate such operations in the plant design so as to minimize the extent of pollution with only minor added cost.

The coal ash separated from the regenerator off-gas amounts to 177,400 lb/hr with only 3.55% carbon, and can be discarded. It is high in sulfur (5.19 wt. %), some of which is in the form of compounds such as calcium sulfide which would give a secondary pollution problem due to release of hydrogen sulfide. Therefore, the process provides for desulfurizing this ash by reacting it with carbon dioxide in the presence of water at 190°F. A sulfur removal of 98% is achieved by this technique. The off-gas, containing hydrogen sulfide, carbon dioxide, and steam is sent to the sulfur plant for clean up.

Carbonated ash amounts to 233,000 lbs. per hour, having picked up considerable weight by adsorption of carbon dioxide in the ash desulfurizer. This carbonated ash is a fine material and must be disposed of without leading to further pollution problems. As of now it appears that the ash can be disposed of by making a slurry with an equal weight of water for return to the mine. Ash from coal preparation will be added to this. Leachability of this material is an area that needs to be defined.

As mentioned, the carbonated ash may be very useful for removing sulfur compounds in other parts of the process, for example, from the vent gas on the lignite dryer and from the raw gas prior to methanation. If such uses are included then the size of the ash desulfurizing system and sulfur plant would be increased accordingly.

### 1.4.7 Auxiliary Facilities

Next to be considered are the liquid and solid effluents from auxiliary facilities. The acceptor process does not use an oxygen plant as do some other gasification processes, nor does it require a utility boiler to provide steam or power for normal operation. All utilities are generated within the process. This of course does not take into account start-up and the requirements of shops or off-site facilities.

The first of the auxiliary facilities to consider is the sulfur plant, which produces free sulfur from gases coming from gas clean-up and ash desulfurizing. A Claus plant is used conventionally for this purpose. Since the total sulfur in the tail gas is relatively small, the tail gas can be incinerated and added to one of the large vent streams. Instead of the Claus plant, other processes could be used such as: Takahax, IFP, or Stretford. Total sulfur production is 119 tpd. It can be sold or stockpiled using well established techniques to avoid environmental problems such as dust and odors.

The next area is waste water treating to remove phenols, ammonia, etc. and suspended solids. This depends on a biox unit and a retention pond for clean-up, as discussed more fully under the section on gas clean-up. A highly desirable objective is to avoid having any net water effluent from the plant and this appears possible for the system as shown, except for water in the ash slurry returned to the mine. The net water available from the retention pond is recycled as water make-up and treated in the make-up water treating facilities.

In view of the large amount of ammonia recovered in the raw gas scrubber it may be that a large part of the hydrogen sulfide will be scrubbed out along with it; if so, little or no separate acid gas removal may be necessary. Information is needed in this area. One possibility that may merit further consideration, is to separate ammonia from $H_2S$ in a sour water stripper, and recycle some ammonia to the gas scrubbing system so as to provide the required $H_2S$ removal.

Treating of make-up water is the next area to be discussed, and will depend on the quality of make-up water at the specific plant location. It may include the use of lime to precipitate hardness and alum to cause flocculation. Sludge from water treating must be concentrated and can be included with the ash disposed of in the mine. Boiler feedwater treating includes demineralization using ion exchange resins. These are regenerated by backwashing with sulfuric acid or caustic which can then be combined, neutralized, and included in the make-up water to the ash slurry scrubbing system.

The final item under auxiliary facilities is the cooling water circuit and cooling tower. Most of the cooling water is used for clean service to condense steam on drivers generating electric power, but a large amount is also used on inter and after coolers on gas compression, as well as for cooling in the gas scrubbing system. The water is recirculated through a cooling tower where it is cooled by evaporating 457,000 lbs per hr of water.

Water circulating to the cooling tower on the utility system will normally need chemical additives to control algae and corrosion. Chromium is considered to be the most effective corrosion inhibitor, but is highly toxic. It can be precipitated out by raising the pH although further study is needed to define the treating needed to assure an acceptable level. Blowdown water from steam boilers is included as makeup to the utility cooling tower. Part of the blowdown or purge from the latter can be recirculated through make-up water treating. Final net purge from the system goes to the ash desulfurizer circuit where it will end up in the slurry being returned to the mine.

As shown, the only net water effluent from the plant is in the ash slurry returned to the mine. A 50% slurry should be satisfactory for handling, corresponding to a water content of 233,000 lbs per hr. This is the effective blowdown from the cooling tower, and is relatively high compared to the amount of water evaporated; therefore, it is expected to be satisfactory as regards total dissolved solids in the cooling tower circuit.

Total water make-up for the plant is 1,383,100 lbs per hr. after crediting the water formed by the methanation reaction. It is possible that most of the moisture in the vent gas leaving the lignite drying operation could be recovered. If so, the net water requirement is reduced to about 700,000 lbs per hr or 1400 gpm, which is unusually low for this plant size.

## 2. SULFUR BALANCE

Of the total sulfur entering in the lignite feed to the plant, 72.4% is recovered as by-product sulfur, another 2.3% is in solid residues and the remaining 25.3% is discharged to the air. The sulfur balance is shown in Figure 7 and summarized in Table 4.

Some concern has been expressed that the sulfur content of the spent acceptor rejected from the gasifier may be high enough under some conditions to cause environmental problems. While low sulfur content has been indicated for normal operation, there may be periods of operation when the rejected acceptor would cause secondary pollution problems upon disposal. Possibly the material could be stockpiled if this occurs, and later reprocessed through the system for clean-up. Or it might be treated in the ash desulfurizing system, although this would increase the $CO_2$ requirements, and provision would have to be made for it in the plant design. Pertinent information should be obtained during pilot plant operations.

Ash containing sulfur is removed from the regenerator and desulfurized by reacting at 190°F with $CO_2$ and steam. These same gas reactants are present in the regenerator and gasifier, although the temperature is much higher, thereby reducing the tendency to strip out sulfur.

In pilot plant operations on the $CO_2$ acceptor processes it will be important to confirm the operation of the sulfur recovery system, so that sulfur in the effluent streams is adequately taken care of.

Table 4

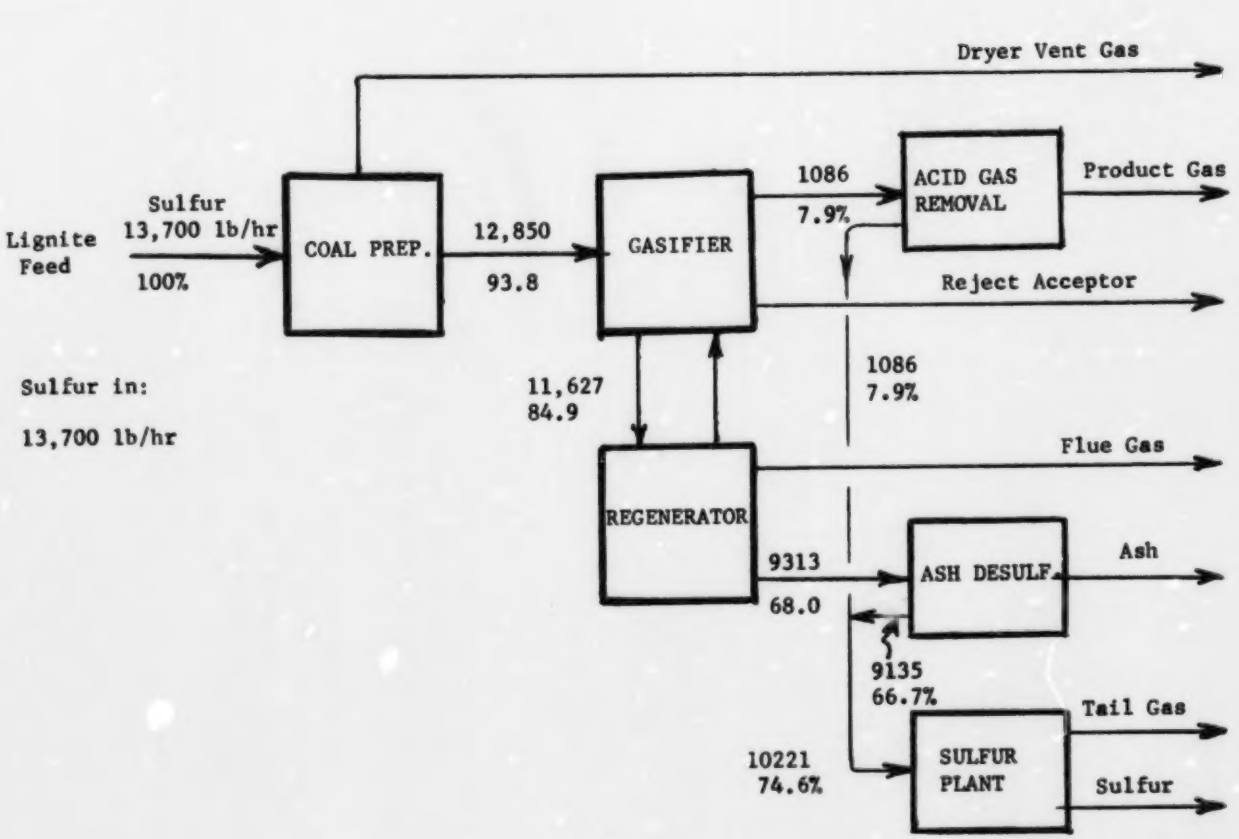
SULFUR BALANCE

| | % |
|---|---|
| By-Product Sulfur | 72.4 |
| Reject Acceptor | 1.0 |
| Spent Ash | 1.3 |
| Regenerator Flue Gas | 16.9 |
| Dryer Vent Gas | 6.2 |
| Claus Tail Gas | 2.2 |
| | 100.0 |

Figure 7

$CO_2$ ACCEPTOR PROCESS

Sulfur Balance




| | lb/hr | % |
|---|---|---|
| Dryer Vent Gas | 850 | 6.2 |
| Product Gas | 0 | 0.0 |
| Reject Acceptor | 137 | 1.0 |
| Flue Gas | 2315 | 16.9 |
| Ash | 178 | 1.3 |
| Tail Gas | 300 | 2.2 |
| Sulfur | 9921 | 72.4 |
| TOTAL Sulfur out lb/hr | 13,700 | 100.0 |

## 3. TRACE ELEMENTS

Fuels burned in the U.S. in 1970 included: 0.5 billion tons of coal, 60 billion gallons of fuel oil, and 100 billion gallons of gasoline. Since the potential contaminants emitted from these sources is so large, EPA and others are making comprehensive studies on the contribution of fuels to pollution by trace components. Available data on trace element contents of fossil fuels have been compiled in reference 12. In addition, surveys are being made to establish the level of contaminants in the environment, and the sources of these. In one study the amount of particulates in urban air was measured, and the concentration of various toxic metals on the particles was determined for particles of different sizes, in the range of 1.5 to 25 microns (13). Results indicate that the concentration of some metals in fly ash is much higher than in the coal. This reference also compares the amount of trace elements in various fuels. Several industrial operations were examined to determine the concentration of elements in the emissions, and this was compared to that in the raw materials. Coal fired power plants were included, giving a basis for examining coal fired furnaces of gasification plants.

The fate of trace elements during combustion was determined in another study for both experimental and industrial furnaces (14). Some 85-90% of the mercury in coal leaves in the flue gas, and is not retained in the ash. Neither is it removed with the fly ash in an electrostatic precipitator. A large portion of the cadmium and lead are also vaporized during the combustion process, but the indications are that these will be retained with the fly ash and can be separated, for example, by an electrostatic precipitator on the stack gas. A water scrubber could be used, although it is not known to what extent trace elements may be soluble. This work also shows that some elements appear in higher concentration in the high density fractions of coal, so that coal cleaning may be effective in some cases for control.

Mass balances were made for 34 elements on a coal fired power station (15). More than 80% of the mercury, a major part of the arsenic, and probably the selenium leave as a vapor. The electrostatic precipitator was about 98% efficient for removing fly ash and the elements associated with it. Analytical techniques and problems are discussed in these references.

It is apparent that further study of the emissions from coal fired boilers associated with gasification plants will be needed with regard to trace elements. However, the necessary studies are just getting underway to define what is emitted, the level that will be acceptable, and control techniques. Therefore it is premature to suggest detailed pollution control procedures at this time. Such a study will be needed in the near future to provide guidelines for coal fired boilers.

Gasification can also release volatile elements from coal, although it may be different than combustion since the atmsophere is reducing. In many gasification processes the maximum temperature is much lower than for combustion, but in others it is comparable. Data have recently been obtained on the decrease in trace metals in the solids as they pass thru the sequence of operations in one gasification process (16). Considerable amounts of many elements are lost from the ash during devolatilization and gasification, especially mercury (see Table 5). The loss is appreciable even in pretreating where the maximum temperature is only 430°C. Preliminary results from this report on bench scale work are summarized below for solids leaving each processing step - the concentration being calculated based on the original weight of coal. Although elements are lost, information is needed as to where they will appear, and in what form (also vapor pressure, water solubility etc). Such results will be needed for critical elements on all gasification processes used commercially, to define what recovery or separation may be required and to allow designing effective pollution control and disposal facilities. It is expected that a large part of volatilized elements will be recovered in the scrubbing operations, and whether this will result in complications or side reactions in the presence of sulfur, phenols, and ammonia, ash, etc., will not be known until further information is available.

Table 5

TRACE ELEMENT CONCENTRATION OF PITTSBURGH NO. 8 BITUMINOUS COAL AT VARIOUS STAGES OF ONE GASIFICATION PROCESS

Calculated on the Raw Coal Basis (From Ref. 16)

| | Feed Coal | After Pretreat | After Hydro-Gasifier | After Electro Thermal Gasifier | % Overall Loss for Element |
|---|---|---|---|---|---|
| Max.Temp.of treat °C | - | 430 | 650 | 1000 | |
| Element: | ppm | | | | |
| Hg | 0.27 | 0.19 | 0.06 | 0.01 | 96 |
| Se | 1.7 | 1.0 | 0.65 | 0.44 | 74 |
| As | 9.6 | 7.5 | 5.1 | 3.4 | 65 |
| Te | 0.11 | 0.07 | 0.05 | 0.04 | 64 |
| Pb | 5.9 | 4.4 | 3.3 | 2.2 | 63 |
| Cd | 0.78 | 0.59 | 0.41 | 0.30 | 62 |
| Sb | 0.15 | 0.13 | 0.12 | 0.10 | 33 |
| V | 33 | 36 | 30 | 23 | 30 |
| Ni | 12 | 11 | 10 | 9.1 | 24 |
| Be | 0.92 | 1.0 | 0.94 | 0.75 | 18 |
| Cr | 15 | 17 | 16 | 15 | 0 |

In operations of the $CO_2$ Acceptor pilot plant, it will be important to obtain information on what happens to trace elements. Some of the volatile ones can be carried out in the gas leaving the gasifier, and since they cannot appear in the pipeline gas, they will have to be removed by the gas cleaning operations. Satisfactory methods for disposal will have to be provided, but in order to do this the first requirement is to obtain data on what elements are carried overhead, and in what form.

Examples of volatile elements are suggested by the preceeding table and in addition carryover can be expected on boron, zinc, fluorine, etc. The form in which they appear may be affected by the gas - thus CO can form carbonyls, and $H_2$ can make arsine, HF, HCl, and $H_3BO_3$. Such reactions have been found in gasification, as well as in other operations at moderate temperature on coal and oil.

When these volatile materials enter the scrubber, they can react further with $NH_3$, $H_2S$ etc. present in the sour water. Information is needed on this to provide a sound basis for defining pollution control and disposal facilities.

Conditions in the regenerator will also tend to remove volatile elements, due to the higher temperature, and large gas volume. It will be important to measure the extent of this, and to obtain data on the extent to which they can be removed by collection in cyclones along with the fly ash.

Trace elements can also leave the system with the fly ash, and in the rejected acceptor. Leachability on these materials needs to be determined, and also on the desulfurized, carbonated ash sent to disposal.

Detailed weight balances around the entire process are needed on all critical trace elements in order to assess the situation, and possible need for controls. Then suitable technology for their separation and disposal can be worked out.

## 4. THERMAL EFFICIENCY

Thermal efficiency is important in that it sets the amount of coal required to produce a given amount of clean fuel gas. Moreover, part of the unrecovered energy in the coal must be dissipated to air or water. As a first calculation the total product gas heating value can be divided by that for the coal fed to the gasifier. This hypothetical figure is 68.5% but it does not allow for the fuel required to dry and preheat the lignite to 500°F; which would lower the efficiency to 62.2%, although sulfur emission would be excessive. It is, therefore, not a realistic number. As a most conservative (lowest efficiency) case it can be assumed that the only fuel fired to the dryer and preheater is low sulfur, low Btu gas taken prior to methanation. This gives a calculated thermal efficiency of 60.2% and is a limiting case in that the vent gas then contains very little sulfur, far below the allowable sulfur emission. If the fuel consisted only of dried lignite fines then sulfur in the vent gas would be 1.6 lbs of $SO_2$ per million Btu fired, compared to the allowable level of 1.2. In order to meet the allowable sulfur level, 75% of the heat required can be supplied by lignite and the other 25% from low sulfur, low Btu gas. This is then a realistic and practical case and gives a thermal efficiency of 61.7%.

An alternative is to burn only lignite in the dryer and preheater, and remove 25% of the sulfur in the vent gas. This might be done by scrubbing with limestone, or used acceptor which could then be returned to the gasifier-regenerator system, and finally processed in the ash desulfurizing unit. For this case, firing only lignite fuel to the coal preparation section, and including allowance for energy used in stack gas clean-up, thermal efficiency is 61.9%. Results on thermal efficiency are shown in Table 6, including numbers for the alternative dryer design shown in Figure 6.

As mentioned earlier, by-product electric power can be made by generating steam at 600 psig and depressuring it through a turbine generator to supply steam required in the gasifier. If credit is taken for this on an equivalent "fuel fired" basis (40,000 KW @ 40% efficiency), thermal efficiency for the process increases by 2.1%. If, in addition, excess steam available from the process is credited, thermal efficiency increases by 5.1%.

It should be noted that this plant design and the calculated thermal efficiency are for a specific basis as given in Table 1 and 2. Methane content of the raw gas from the gasifier is only 6.08 Vol. % on a dry basis, even though the hydrogen content is quite high (70.91 vol. %) as a result of the shifting effect associated with $CO_2$ removal by the acceptor. The developer has indicated that pilot plant data show methane contents in the gasifier product about twice that given in Table 1. This would increase all of the thermal efficiencies given in Table 6, but the exact amount has not been calculated.

## Table 6

## Thermal Efficiency

| Base Design | lb/hr | MM Btu/hr |
|---|---|---|
| In | | |
| Lignite to gasifier | 1,368,000 | 15,212 |
| Lignite to Coal prep. | 165,470 | 1,546 |
| | | 16,758 |
| Out | | |
| Pipeline Gas | -- | 10,417 |
| Base Thermal Efficiency $\frac{10,417}{16,758}$ = | | 62.2% |
| If use only low Btu gas as fuel to coal prep., efficiency = | | 60.2% |
| Alternative dryer design of Figure 6 | | |
| Efficiency as shown gas/coal fuel | | 62.4% |
| - plus credit for by-product power | | 64.5% |
| - and credit for by-product steam | | 67.5% |
| Efficiency if make only low Btu gas | | 76% |

Although this study is based on making SNG, it appears that the process can also be used to make a low-Btu clean fuel gas (19). An estimate of thermal efficiency for such a case was made by backing out the methanator, giving 76% efficiency. It appears that the process might also be able to give adequate sulfur removal at high temperature - without having to cool to water scrubbing temperatures. If so, thermal efficiency might be credited with sensible heat in the low-Btu gas, provided the moisture content is low enough so that water does not have to be removed from the gas.

In any process making SNG from syngas, the maximum theoretical thermal efficiency is limited to 81% by the heat released in the methanation reaction. Therefore, it is obviously much more efficient to use low-Btu gas where applicable and wherever possible for large consumers, industrial uses, etc.

# 5. POSSIBLE PROCESS CHANGES

## 5.1 Process Alternatives Considered

The gasification process was examined to indicate what facilities should be added to control pollution, or whether simple modifications could be made to the process to eliminate or minimize the problems. Some of the alternatives considered are summarized in Table 7, classified according to the section of the process involved.

The general approach in this study was a stepwise attack as follows:

1. Eliminate the problem if possible by simple modification of the design.
2. Provide additional pollution control facilities where needed.
3. Increase thermal efficiency of the process by minor changes.
4. Point out where further work is needed to resolve pollution questions, or where it could improve the operations significantly.

Examples of alternatives in each of the above four catagories will now be given.

On item 1 an example is the consideration of type of fuel to use in coal drying. If lignite fines are used exclusively as suggested by the developer then sulfur in the flue gas is undesirably high. An alternative is to use only low Btu gas from a point just ahead of the methanator and after sulfur has been removed, but this is a more expensive fuel and leaves no place in the plant to use the lignite fines. It does give minimum sulfur emission in the vent gas. A reasonable compromise is to supply 25% of the fuel requirement as low Btu,low sulfur gas, and the other 75% as lignite fines.

An example of additional pollution control equipment needed is on the regenerator flue gas leaving the turbine, where dust control facilities may be required. Only cyclones have been provided and experience on power plants shows that fly ash recovery in cyclones is not adequate. We have included an electrostatic precipitator for this purpose although a scrubbing system could be used instead. In addition, waste water treating facilities were added because of residual ammonia, phenols, etc. that must be removed.

On item 3, thermal efficiency can be increased by burning residual carbon monoxide in the regenerator flue gas. It could be burned in a conventional CO boiler after the turbine, but the temperature at this point is so low that it would be necessary to fire additional fuel in order to maintain stable combustion. A much more efficient alternative is to burn the carbon monoxide before the turbine to reheat the flue gas, pass it through a boiler to generate additional steam, and then to the turbine.

## Table 7

## PROCESS ALTERNATIVES CONSIDERED

Coal Dryer:

- Coal fired with flue gas desulfurizing versus use low Btu fuel gas from process.
- Recover dust by electrostatic precipitator or scrubber versus bag filters.

Gas Clean-Up:

- Air-fin coolers to minimize cooling water required.

Acid Gas Removal:

- Stretford, IFP, or Takahax process to remove $H_2S$ selectively versus amine or carbonate scrubbing.

Methanator:

- Ways to generate high pressure steam from heat released in reaction.

Regenerator:

- Scrub flue gas from turbine to remove dust versus electrostatic precipitator.
- Burn carbon monoxide before turbine versus CO boiler after turbine.

Ash Desulfurizer:

- Supply $CO_2$ by scrubbing exhaust gas from turbine, versus scrubbing sulfur plant tail gas to recycle $CO_2$. (Enough $CO_2$ can not be made available from gasifier products.)

Areas where additional work is required (item 4 above), include: (a) the technique for selectively removing sulfur from the raw gas without removing a large amount of carbon dioxide, (b) the system needs further definition as regards ash disposal and potential secondary pollution from leaching, etc., (c) further information on potential odors is needed on the lignite dryer, ash, reject acceptor, and water treating, (d) the fate of trace elements in the process must be defined and may be rather different than experienced in other gasification processes which do not use dolomite acceptor.

## 5.2 Engineering Modifications

In the course of the study, some additions and modifications were made in order to have the process complete and self-sufficient, or to improve efficiency, or help control emissions. Where these use only known techniques that do not need experimental development, they are referred to as engineering modifications and are shown in Table 8.

On the coal dryer, for example, water could be recovered from the vent gas since it contains 800,000 lbs per hr. This is large relative to the net requirement of 1,383,100 lbs per hr. of water make-up. Most of the water in the dryer vent gas could be recovered by cooling the gas in air-fin coolers after the bag filters, e.g. to about 150°F, which would add investment but not require cooling water, and may be an attractive way to produce a large part of the make-up water. Fluid bed drying may be attractive versus the pneumatic system shown in that it should allow a closer temperature approach.

The technique of cooling the reject acceptor leaving the gasifier was not specified, and therefore, we have added a conventional fluid bed cooler in which steam is generated, followed by water sprays to cool the solids further while still leaving a dry product. The same technique is used to cool spent ash leaving the regenerator.

The $CO_2$ Acceptor Process is unusual in that it does not require either shifting or $CO_2$ removal ahead of methanation. This allows much greater flexibility in considering what acid gas removal process to use for the specific application. The usual amine scrubbing or hot carbonate systems will tend to remove more $CO_2$ than desired when removing sulfur to a very low level, therefore, they are not particularly well-suited for this use. However, absorption/oxidation type processes could be much more attractive. In these $H_2S$ is selectively absorbed in a solution where it is catalytically oxidized to free sulfur, which is removed as a by-product. Such processes are offered by IFP, Stretford, and Takahax etc., and would not remove $CO_2$.

The methanator system was not described by the developer and neither was the technique for recovering waste heat from it. We have used this heat to generate high pressure steam and have also included in the water balance the water produced by the methanation reaction.

## Table 8

## ENGINEERING MODIFICATIONS

**Coal Preparation:**

- Fluid bed dryer versus pneumatic system.
- Recover water from vent gas by using air-fin coolers.

**Gasifier:**

- Cool reject acceptor in fluid bed to generate steam and minimize cooling water.

**Regenerator:**

- Burn carbon monoxide before flue gas turbine to recover high level heat, rather than use conventional CO boiler after the turbine.

**Sulfur Plant:**

- Use low temperature liquid absorption/oxidation reaction to form sulfur directly from gases leaving ash desulfurizer and acid gas removal, and avoid Claus unit.

**Utilities:**

- Generate all steam at high pressure, and depressure through bleeder turbines to generate electric power, then use depressured steam in gasifier.

In general, the waste heat of the process will go either to air or to water. In a typical cooling tower only 20% to 30% of the heat is taken out as sensible heat of the air flowing through. The other 70-80% of the heat is removed by evaporation of water in the cooling tower. This is by far the major water consumer in the entire process; thus,for a plant with no net water effluent the total water consumption for the plant will be primarily set by the thermal efficiency, or rather the thermal inefficiency. One way to reduce water consumption is to transfer more of the waste heat to air as sensible heat using air fin exchangers. Normally, this raises the investment and decreases thermal efficiency but at least partial application may be justified for reducing water consumption and potential water pollution where there is an effluent. Air fins are more suitable for removing higher level heat such as above 150°F. For low temperature services such as on the steam condensers of turbine drivers, where the condensing temperature may be only 105°F, it may not always be practical to use air fins.

## 5.3 Potential Process Improvements

Some of the possible changes in the process have potential for significant improvement but would require further study and perhaps experimental work. These are shown in Table 9.

One promising possibility is to use the acceptor to remove sulfur from other screams in the process. It is known that it will retain sulfur under conditions in the gasifier and regenerator, and that it can be regenerated to remove sulfur. Thus, sulfur and dust emissions from the dryer could be controlled by scrubbing with a slurry of the acceptor, which would then be recirculated to the gasifier-regenerator, and the ash desulfurizing system for regeneration.

A similar operation could be used on the raw gas from the gasifier and would have an additional advantage if it would take out sulfur and not much carbon dioxide. It could also be used on the flue gas leaving the expander turbine. Although this gas is already low in sulfur, it contains dust which could be removed by scrubbing, while at the same time the scrubbing operation would reduce sulfur level at little added cost.

An alternative to consider for removing sulfur from the raw gas is to use a low temperature absorption-oxidation type reaction to selectively remove sulfur, as is offered by Stretford, IFP, and Takahax. These processes use a scrubbing liquid containing a catalyst to convert hydrogen sulfide directly to elemental sulfur, which is then separated. They give little or no removal of carbon dioxide. Sulfur compounds other than $H_2S$ may be present but could probably be hydrolyzed to $H_2S$ over a suitable catalyst at about 500 to 700°F as the raw gas is being cooled.

Table 9

POTENTIAL PROCESS IMPROVEMENTS

Coal Preparation:

- Use recirculated acceptor to remove sulfur from vent gas and supply all heat requirement by burning lignite fines. Return acceptor to gasifier-regenerator system.

Gas Clean-Up:

- Use recirculated acceptor to remove sulfur from raw gas without removing $CO_2$.
- Use low temperature liquid absorption/oxidation reaction to form sulfur directly, instead of scrubbing with amine or carbonate.

Methanator:

- Fluid bed or slurry type reactor, or catalytic tube wall of Bureau of Mines to improve heat recovery versus fixed bed with gas recirculation through waste heat boiler.

Other:

- Use process to make low sulfur - low Btu gas for combined cycle power generation.

A final point for discussion is the use of the Acceptor process to provide a low Btu low sulfur gas fuel at high temperature and under pressure for power generation or other uses. This process offers one way to desulfurize gas at high temperature, instead of cooling it and scrubbing at say 200°F or less. It could, therefore, be an efficient way to make low sulfur fuel gas from coal and alleviate the difficult pollution control problems of burning coal directly (11). The hot gas might be used in a combined cycle where it is first burned for use in a gas turbine, and the hot effluent then goes to a conventional steam boiler. Overall efficiency to electric power for such a process could be over 45%.

In gas turbine applications at present, there are strict limitations on the dust loading due to erosion of turbine blades. Typical specifications are for 30 wt ppm or less of solids content in the fuel gas burned to supply the turbine, with a maximum particle size of 10, or in some cases 2 microns. Corrosion is also a major concern. Considerable development work is underway in this field, therefore the situation should be reviewed periodically, since the incentive for application of turbines can be very large.

## 5.4 Process Details

Other details on the process are covered in Tables 10 through 16.

## Table 10

## COMPOSITION OF LIGNITE FEED AND PRODUCT GAS

### Lignite Feed

Proximate analysis: Wt. %

| | |
|---|---|
| Moisture | 33.67 |
| Volatile<br>Fixed Carbon | 58.86 |
| Ash* | 7.47 |
| | 100.00 |

Ultimate analysis, Moist. free wt. %

| | |
|---|---|
| C | 62.87 |
| H | 4.20 |
| N | 1.04 |
| S | 0.89 |
| O | 20.14 |
| Ash | 10.86 |
| | 100.00 |

High Heating Value* 10,945 Btu/lb

### Product Gas Composition (dry) Mol. %

| | |
|---|---|
| $CH_4$ | 93.00 |
| $H_2$ | 4.84 |
| CO | .10 |
| $CO_2$ | 1.31 |
| $N_2$ | 0.75 |
| | 100.00 |

* Calc. to be equiv. to specified properties after preheater (Table 1), with 1.6 wt. % loss in preheater and no loss in ash or heating value.

Table 11

STEAM BALANCE

| | lb./hr. | |
|---|---|---|
| | 600 psig steam | 165 psig steam |
| **Steam Generated** | | |
| Net From Flue Gas Including CO Burner | 567,000 | -- |
| Gasifier Waste Heat Boiler | 525,000 | 190,000 |
| Methanator | 840,000 | 210,000* |
| From Cooling Reject Acceptor and Ash | -- | 63,000 |
| | 1,932,000 | 463,000 |
| **Steam Consumed** | | |
| Gasifier | -- | 1,653,700 |
| Power Generation | 175,000 | -- |
| Amine Scrubbing | -- | 63,000 |
| Water Treating | -- | 126,000 |
| | 175,000 | 1,842,700** |

* From bleeder turbine on gas recycle compressor.

** Total steam generated is more than required for gasification, and can easily be run through a bleeder turbine-generator to supply power to mine, shop facilities, offices, etc. and produce the 165 psig steam required. Surplus steam available is then 377,000 lb/hr at 165 psig.

Table 12

WATER REQUIREMENTS

| Water Consumed | lb/hr |
|---|---|
| By reaction in gasifier | 1,053,000 |
| In wet ash rejected | 233,000 |
| To ash desulfurizer | 15,800 |
| Evap. in cooling tower | 457,000 |
| Drift loss in cooling tower | 43,000 |
| Handling loss on condensate | 68,000 |
| TOTAL Consumed | 1,869,800 |
| Available from methanator | 483,000 |
| Available from gas Compres. | 3,700 |
| TOTAL Available | 486,700 |
| Net make-up required | 1,383,100 (2766)* |

* If the moisture in the vent gas were recovered (as discussed), the make-up would be about half as much, i.e. 1400 gpm.

Table 13

POWER CONSUMPTION

| Consumer | KW |
|---|---|
| Coal preparation | 12,800 |
| Scrubber | 600 |
| Acid gas removal | 100 |
| Gasifier and regenerator | 100 |
| Ash desulfurizer | 300 |
| Sulfur plant | 400 |
| Methanator | 100 |
| Cooling water pumps | 1,500 |
| Cooling water fans | 1,000 |
| Dolomite prep. | 600 |
| | 17,500* |

* This power is available from the process scheme discussed (see page 20).

## Table 14

## LIGNITE AND FUEL CONSUMED

| | |
|---|---|
| Lignite to Preheater (moist. free) | 1,436,400 lb/hr |
| Lignite fuel to coal prep. (moist. free) | 86,870 lb/hr |
| Gas to coal prep. (low Btu)* | 341 MM Btu/hr |
| Sulfur Plant tail gas incin. | 22 MM Btu/hr |

* Equivalent to 32,000 lb/hr moist. free lignite

## Table 15

### POTENTIAL ODOR EMISSIONS

Coal preparation dryer, and preheater
Wet ash disposal
Reject acceptor disposal
Regenerator flue gas
Sulfur plant
Ponds, waste water treating ($NH_3$, etc.)
Trace phenols from gas clean-up.

Table 16

MISCELLANEOUS INPUTS

| | |
|---|---|
| For water treating: | lime, caustic, alum, sulfuric acid, chlorine |
| Cooling water additives: | anti-algae (chlorine)<br>anti-corrosion (chromium salt) |
| Other chemicals: | amines and additives<br>glycol for drying product gas |
| Catalysts, etc.: | methanation catalyst<br>Claus plant catalyst<br>ZnO guard bed to remove sulfur |
| Oil: | to lubricate pumps, compressor, etc. |

## 6. TECHNOLOGY NEEDS

An objective of EPA is to anticipate pollution problems and call attention to them ahead of time so that they can be examined carefully, and planning or experimental work carried out where a need is indicated. This approach is intended to:

1. Point out to process developers where pollution problems may appear, to allow resolving questions well before definite plans are underway on commercial applications.

2. Encourage or support work needed to develop techniques or processes aimed at pollution control - especially when it applies to problems that are common to a number of fuel conversion processes, or where existing technology is inadequate.

3. Identify pollution areas that are not yet adequately defined or controlled, and point out what further work is needed.

An important part of the present study is to review various gasification processes to identify items of the above types. Results from examination of this gasification process, are summarized in accompanying Table 17 grouped according to the process area.

Illustrating the first point is sulfur control on the dryer vent gas when burning lignite. As pointed out earlier, sulfur emission can be controlled by using some low sulfur gas made in the process, although this increases the amount of lignite that must be gasified. An alternative is to scrub flue gas leaving the dryer to remove sulfur. A number of suitable processes are currently undergoing large scale testing, some of which include regeneration of the scrubbing medium to produce by-product sulfur, sulfuric acid, or gypsum. An advantage for flue gas cleanup is that 100% of the heating value of lignite is then available for drying, versus about 70% when the lignite is gasified to make clean fuel gas. Scrubbing can also remove fly ash or dust, and avoid the need for bag filters. It is apparent that there is a great need for effective processes to clean up stack gas from combustion operations.

Referring to item 2 above, a common problem for most coal gasification processes is the methanation operation. Thermal efficiency is only 81% in this case, resulting in a very high heat release, which it is important to recover, for example, as high pressure steam. One approach is to use a series of fixed beds having gas recirculation through waste heat boilers. Alternatives are to use a fluid bed or slurry type methanation reactor with steam regeneration coils in the reactor.

Regarding item 3 above, there is a question as to the leachability of salts and trace metals in the rejected ash and acceptor. These are unknown areas in which further work is needed to define the problem. Also a suitable outlet for the reject acceptor needs to be developed and hopefully it can be shown to be suitable for land

Table 17

TECHNOLOGY NEEDS

Coal Preparation:

- Simple sulfur clean-up on vent gas to allow using coal fines alone as fuel to dryer, with no high value gas fuel.
- Recover water from dryer vent gas when using high moisture western coal.

Gasification:

- Operation to assure no formation of tars, phenols, etc. that complicate clean-up.
- Use for spent acceptor; leachability, trace metals.

Gas Clean-Up:

- Ways to remove sulfur compounds without removing $CO_2$.
- Detailed information on kinds and amounts of solids, oil, sulfur and nitrogen compounds, and other minor components in raw gas and effluents during normal operation as well as during upsets - their separation, and disposal.
- Hydrolysis of sulfur compounds such as COS to $H_2S$ prior to sulfur removal. Presence of cyanides, thiocyanates etc.
- Presence of trace compounds: HF, arsine, metal carbonyls, etc.
- High temperature clean-up of sulfur and dust.

Methanator:

- Designs to maximize recovery of heat to make high pressure steam (e.g. optimum reactor temperature and cooling technique).

Regenerator:

- Efficient dust removal from flue gas.
- Development work, if required for flue gas turbine to maximize energy recovery.
- Content of sulfur, trace elements, metal carbonyls, odors, in flue gas.

Ash Desulfurizer:

- Use and disposal of ash and spent acceptor - leachability, trace metals.

fill. Other areas that are not yet adequately defined have already been discussed, for example, the exact technique for removing sulfur from the raw gas without removing much $CO_2$.

Finally, the very large incentive to use gas turbines for energy recovery should be emphasized again, and since this often involves operating on dusty or corrosive gases, development of suitable technology could lead to more extensive use. The need is for a process to clean up hot gases, and particularly to remove various sulfur compounds and small particles. If such a technique were commercially available and practical, it could be used to advantage in the $CO_2$ Acceptor process to clean-up the raw gas from the gasifier prior to methanation. This would avoid the inefficient cooling, scrubbing, and reheating that is now required.

## 7. QUALIFICATIONS

As pointed out, this study does not consider cost or economics. Also, areas such as coal mining and general off sites are excluded, as well as miscellaneous small utility consumers such as instruments, lighting etc. These will be similar and common to all coal conversion operations.

The study is based on the specific process design and coal type supplied by the process developer, with modifications as discussed. Plant location is an important item of the basis and is not always specified in detail. It will affect items such as the air and water conditions available, and the type of pollution control needed. For example, the $CO_2$ Acceptor study is for low sulfur western coal since the process is not suited for use with eastern coals. Because of variations in coal feed, moisture content, and other basis items, great caution is needed in making comparisons between coal gasification processes as they are not on a completely comparable basis. Some of the important factors in the study basis that must be specified in order to make an engineering analysis of a process are summarized in Table 18.

Other gasification processes may make large amounts of various by-products such as tar, naphtha, phenols, and ammonia. The disposition and value of these must be taken into account relative, to the increased coal consumption that results and the corresponding improvement in overall thermal efficiency. Such variability further increases the difficulty of making meaningful comparisons between processes.

The $CO_2$ Acceptor process makes no appreciable amounts of tar, naphtha, or phenols; however, there is a sizeable yield of ammonia amounting to 130 tpd and it is assumed that this can be recovered and sold.

## Table 18

## GENERAL SELECTION OF STUDY BASIS

**Location:** Air and water conditions, water treatment, rainfall.

**Coal:** Type, preparation, drier type and fuel ash disposal.

**By-Products:** Tar, phenols, naphtha, ammonia, etc.

**Utilities:** Pollution control on boiler
Fuel to boiler
Water quality and treatment
Cooling water additives
Cooling tower operation (fog and drift)
Application of air-fin coolers

**Minor Components:** Cyanides, ammonia, various sulfur compounds, and products of interactions.

**Trace Components:** e.g. mercury, arsenic, fluorine

## 8. BIBLIOGRAPHY


1. Mosher, D. R. et al "Basic Features of the $CO_2$ Acceptor Gasification Process" ACS Div. Fuel Chem., September 1971.

2. Fink, C. E., et al "$CO_2$ Acceptor Process - Status of Development" 1973 Lignite Symp. Grand Forks ND, May 9-10, 1973.

3. Clancey, J. T., et al "Pipeline Gas from Lignite Gasification" R&D Rept. No. 16 - Interim Report No. 4, by Consol. Coal Co. for OCR, May 9, 1969.

4. Letter from G. P. Curran of Consolidation Coal Co. to ERE of December 5, 1973.

5. Coalgate, J. L., Akers, D. J. and From, R. W. "Gob Pile Stabilization, Reclamation, and Utilization", OCR RE'D Report 75, 1973.

6. Parrish, R. W. and Neilson, H. B., "Synthesis Gas Purification Including Removal of Trace Contaminants by the BENFIELD Process", presented at 167th National Meeting of ACS, Div. of I&EC, Los Angeles, March 31-April 5, 1974.

7. Valentine, J. M., "Purification of SNG with Selexol", ibid.

8. Kniebel, M., "Rectisol and Purisol Process for Syn-Gas Purification", ibid.

9. Atmospheric Emissions from Petroleum Refineries, U.S. Dept. of Health, Educ. and Welfare, Public. No. 763, 1960.

10. Ohio State University,"Acid Mine Water", PB 199835, for EPA, April 1971.

11. "Control Techniques for $SO_x$ Air Pollution", Rept. AP-52, U.S. Dept. Health, January 1969.

12. Magee, E. M., Hall, H. J. and Varga, G. M. Jr., "Potential Pollutants in Fossil Fuels", EPA-R2-73-249, NTIS PB No. 225,039, June 1973.

13. Lee. R. E., et al., "Trace Metal Pollution in the Environment", Journ. of Air Poll. Control, 23, (10), October, 1973.

14. Schultz, Hyman et al., "The Fate of Some Trace Elements During Coal Pre-treatment and Combustion", ACS Div. Fuel Chem. 8, (4), p. 108, August, 1973.

15. Bolton, N. E., et al., "Trace Element Mass Balance Around a Coal-Fired Steam Plant", NCS Div. Fuel Chem., 18, (4), p. 114, August 1973.

16. Attari, A. "The Fate of Trace Constituents of Coal During Gasification", EPA Report 650/2-73-004, Aug., 1973.

17. Franzel, H. L. "Refiner Cuts Energy Use Sharply" Oil Gas Journal June 10, 1974, pages 58-61.

18. The Environmental Impact of Coal-Based Advanced Power Operating Systems, F. L. Robson and A. J. Giramonti, EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, Mo., May 13-16, 1974.

19. Sulfur Emission Control with Limestone/Dolomite In Advanced Fossil Fuel Processing Systems, D. L. Keairns, E. P. O'Neill, D. H. Archer, EPA Symposium on Environmental Aspects of Fuel Conversion Technology St. Louis, Mo., May 13-16, 1974.